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TO JULY 1, 1968

by

Herbert H. Hyman and Cedric L. Chernick

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Chemistry Division

October 1968

INTRODUCTION

In this bibliography the entries are arranged by year (1962 through 1968). Within each year, the entries are arranged alphabetically according to the name of the first author.

Most entries cite accounts in journals and books in the conventional way, but also cited are a number of USAEC reports and a few foreign reports. The symbols and corresponding originating institutions are as follows:

AERE - United Kingdom Atomic Energy Research Establishment
ANL - Argonne National Laboratory
BNL - Brookhaven National Laboratory
CEA - Commissariat a l'Energie Atomique (France)
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In general, copies of theses, a few of which are cited, are available from University Microfilms, 300 N. Zeeb Road, Ann Arbor, Michigan 48106.

62-1. Allen, Leland C.

BINDING OF INERT GAS HALIDE MOLECULES, Science **138**, 892-3 (1962).

An electronic explanation of the existence of noble gas halides and predictions of the properties to be expected of these compounds are presented.

62-2. Allen, Leland C., and William D. Horrocks, Jr. CONVENTIONAL ELECTRON PAIR DESCRIPTION OF XENON COMPOUNDS, J. Am. Chem. Soc. **84**, 4344-5 (1962).

XeF_4 has 12 electrons which are assumed to participate in molecular binding. The outer octet of Xe yields 8 electrons and each F supplies 1. The simple conventional nature of the compound predicts a conventional length for the Xe-F bond, $1.33 + 0.64 = 1.97 \text{ \AA}$. XeF_2 is also known to exist, and molecular binding involves 10 electrons, either 8 from Xe and 2 from the F, or 4 from each. Five electron pairs are formed, whereas in XeF_4 , the 12 electrons form 6 electron pairs. Orbital symmetry around Xe can be designated as sp^3d or sp^3 . XeF_2O , XeF_2O_2 , and XeF_2O_3 are all predicted with equal a priori probability.

62-3. Bartlett, Neil

XENON HEXAFLUOROPLATINATE, Proc. Chem. Soc. **1962**, 218.

Xenon was shown to react at room temperature with platinum hexafluoride to form $\text{Xe}^+\text{PtF}_6^-$. The compound is an orange-yellow solid which has negligible vapor pressure at room temperature, but which sublimates when heated under vacuum. The sublimate hydrolyzes rapidly when treated with water vapor:
 $2\text{XePt}_6 + 6\text{H}_2\text{O} \rightarrow 2\text{Xe} + \text{O}_2 + 2\text{PtO}_2 + 12\text{HF}$.

62-4. Chernick, C. L., H. H. Claassen, P. R. Fields, H. H. Hyman, J. G. Malm, W. Manning, M. S. Matheson, L. A. Quarterman, F. Schreiner, H. H. Selig, I. Sheft, S. Siegel, E. N. Sloth, L. Stein, M. H. Studier, J. L. Weeks, and M. H. Zirin

FLUORINE COMPOUNDS OF XENON AND RADON, Science **138**, 136-8 (1962).

Xenon and fluorine combine readily. Xenon tetrafluoride is a colorless crystalline material, stable at room temperature. The existence of at least one other fluoride and two oxyfluorides was demonstrated. The heaviest "inert gas," radon, also reacts with fluorine, yielding a compound less volatile than xenon tetrafluoride.

62-5. Claassen, H. H., H. Selig, and J. G. Malm

XENON TETRAFLUORIDE, J. Am. Chem. Soc. **84**, 3593 (1962).

Xe and F_2 were found to react readily under certain conditions to form XeF_4 , a stable solid which does not melt up to 100°C . The method of preparation comprises heating a mixture of 1 part Xe and 5 parts F_2 to 400°C for 1 hr and then rapidly cooling the mixture to room temperature. Some of the physical and chemical properties of XeF_4 are described.

62-6. Fields, Paul R., Lawrence Stein, and Moshe H. Zirin

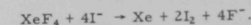
RADON FLUORIDE, J. Am. Chem. Soc. **84**, 4164-5 (1962).

The reaction of trace amounts of radon with fluorine was studied. It was found that radon forms a stable fluoride which is less volatile than XeF_4 . The composition of the radon fluoride was not determined. The fluoride can be reduced with hydrogen quantitatively to recover elemental radon. At 200°C the compound appeared to be stable in hydrogen, but at 500°C and a hydrogen pressure of 800 mm it was completely reduced within 15 min. The tracer quantities of radon fluoride prepared showed no evidence of radiation decomposition from alpha-particle emission.

62-7. Holloway, J. H., and R. D. Peacock

A SIMPLE PREPARATION OF XENON TETRAFLUORIDE, Proc. Chem. Soc. **1962**, 389-90.

Xe gas (500 ml) was allowed to diffuse into a stream of hydrogen fluoride-free fluorine which was flowed slowly (6 l/hr) through a 4-ft length of nickel tube (of 1/2-in. OD) packed with nickel sheet. The center of the tube was heated to a dull-red heat. The gas stream passed from the tube through three successive U-tubes. The first, cooled to -78°C , trapped the xenon tetrafluoride; the others were cooled to -180°C to trap any unreacted xenon. The composition of the compound was established by studying the reaction



62-8. Hoppe, R., W. Dähne, H. Mattauch, and K. Rödder

FLUORINATION OF XENON, Angew. Chem. Intern. Ed. **1**, 599 (1962). [Original paper in German, Angew. Chem. **74**, 903 (1962).]

Xenon fluoride was prepared by mixing commercial Xe with carefully purified fluorine (prepared electrolytically) in a $\text{Xe}:\text{F}_2$ proportion of 1:2 by volume in a sealed quartz vessel and subjected at room temperature to discharges from an induction coil. The XeF_2 initially formed was plainly unstable and disproportionated into Xe and a compound containing more fluorine, probably XeF_4 .

62-9. Maričić, S., and Z. Vekšić

FLUORINE MAGNETIC RESONANCE IN XENON TETRAFLUORIDE, Croat. Chem. Acta. **34**, 189-90 (1962).

Below 237°K the spectra became asymmetric with a shape characteristic of substances with paramagnetic properties. Above this temperature the line shapes were symmetric with a second moment between 3.5 (at 237°K) and 2.7 G (at 293°K). The latter values are discussed in relation to the molecular structure of xenon tetrafluoride.

62-10. Marsel, J., and V. Vrščaj

MASS SPECTROMETRIC MEASUREMENTS OF XENON FLUORIDES, Croat. Chem. Acta. **34**, 191-3 (1962).

The spectra were recorded with a modified Nier-type spectrometer. It was found necessary to introduce the sample vapors continuously for 48 hr in order to drop the Xe^+/XeF^+ ratio from 100:1 to 5:1. The masses in

the spectral range above the position corresponding to XeF_4 are suggested to be due to XeOF_4 , XeOF_3 , XeOF_2 , or higher xenon fluorides up to XeF_8 .

62-11. Slivnick, J., B. Brčić, B. Volavšek, J. Marsel, V. Vrščaj, A. Šmalc, B. Frelec, and Z. Zemljič
ON THE SYNTHESIS OF XeF_6 , Croat. Chem. Acta. **34**, 253 (1962). (In German.)

An attempt was made to fluorinate Xe with the purest fluorine in excess at 700°C and at approximately 200 atm. The product was cooled to -78°C and the excess F_2 pumped out. The residue was sublimed in vacuum. The first fraction melted at 25°C to a pale yellow liquid. It was stable under vacuum in glass ampules, but exploded very violently in air or under impact. Analysis showed the F/Xe ratio to be 6.1 ± 0.3 , corresponding to a composition of XeF_6 . Mass-spectrometric studies confirmed this composition.

62-12. Slivnik, J., B. Brčić, B. Volavšek, A. Šmalc, B. Frelec, R. Zemljič, A. Anžur, and Z. Veksl

ON THE SYNTHESIS OF AND MAGNETIC MEASUREMENTS ON XENON TETRAFLUORIDE, Croat. Chem. Acta. **34**, 187-8 (1962).

The synthesis of XeF_4 was verified and more details of the preparation are given. Xenon (at 1 atm) and fluorine (at 3 atm) were introduced into a 850-ccm Monel metal reaction vessel. A special construction of a vacuum-tight valve withstanding 150 atm was used. The reaction was completed after 3 hr at 400°C. Magnetic susceptibility measurements indicate a temperature-dependent diamagnetism, becoming less negative below 240°K.

62-13. Weeks, James L., Cedric L. Chernick, and Max S. Matheson

PHOTOCHEMICAL PREPARATION OF XENON DIFLUORIDE, J. Am. Chem. Soc. **84**, 4612-13 (1962).

Xenon difluoride was prepared in relatively pure form by the photochemically induced reaction of xenon and fluorine at room temperature. Infrared spectra of the products of some irradiations showed an intense band with peaks at 549 and 565 cm^{-1} due to XeF_2 , and showed no absorption at 590 cm^{-1} , where XeF_4 has a strong absorption. XeF_2 is a solid at room temperature and easily forms crystals which can be made to sublime readily or to grow on a slightly cooled wall of a containing vessel. Room-temperature powder patterns indicate that the cell is body-centered tetragonal with $a = 4.316$ and $c = 6.993$ kx. It appears to have a room-temperature vapor pressure of about 2 mm.

1963

63-1. Agron, P. A., G. M. Begun, Henri A. Levy, A. A. Mason, C. G. Jones, and D. F. Smith

XENON DIFLUORIDE AND THE NATURE OF THE XENON-FLUORINE BOND, Science **139**, 842-4 (1963).

Xenon reacts with fluorine to form XeF_2 , which can be isolated before it reacts with fluorine to form XeF_4 . The linear configuration of XeF_2 with the 2.00-Å bond length and the vibrational force constants support the assignment of 10 electrons to the valence shell of

xenon. Similar arguments support the assignment of 12 and 14 valence electrons, respectively, to xenon in XeF_4 and XeF_6 .

63-2. Allen, Leland C.

BINDING OF XENON TO HALOGENS, TO ALKALI METALS, AND TO ITSELF, Nature **197**, 897 (1963).

Properties of Xe that influence the binding of Xe to halogens, to alkali metals, and to itself are discussed. It is pointed out that theoretical prediction of inert gas compounds is not adequate.

63-3. Allen, Leland C.

THEORY OF BINDING IN INERT-GAS MOLECULES, pp. 317-28 of "Noble-Gas Compounds," Chicago, Univ. of Chicago Press, 1963.

A many-electron theory for binding in inert-gas molecules is formulated and discussed. The importance of instantaneous electron-electron correlation in specifying the relationship between the periodic table and molecular formation is pointed out. A survey of other theoretical efforts and their relation to the present is also included.

63-4. Appelman, Evan H.

CHARACTERIZATION OF OCTAVALENT XENON IN AQUEOUS SOLUTION, pp. 185-90 in "Noble-Gas Compounds," Chicago, Univ. of Chicago Press, 1963.

Aqueous solutions of Xe(VIII) have been prepared from the solid sodium perxenate obtained by alkaline hydrolysis of XeF_6 . At high pH these solutions decompose slowly to Xe(VI) and oxygen, the rate increasing with decreasing pH. The standard potential in basic solution for the Xe(VI) - Xe(VIII) couple is estimated to lie between 0.7 and 1.24 V. The ultraviolet spectrum of Xe(VIII) is given as a function of pH, and potentiometric acid-base titrations of both Xe(VIII) and Xe(VI) are presented. A series of protonation equilibria is postulated to explain the observations.

63-5. Bartlett, Neil

NEW COMPOUNDS OF NOBLE GASES: THE FLUORIDES OF XENON AND RADON, Am. Scientist **51**, 114-18 (1963).

Synthesis of xenon di-, tetra-, and hexafluoride and radon difluoride is described, and properties of the compounds are discussed. Radon difluoride was prepared by heating a radon-fluorine mixture to 400°C for 30 min. It is much less volatile than its Xe analog, and has resistance to reduction by H, which occurs only above 200°C. The hydrolytic behavior of XeF_4 points to the existence of hydrated oxides and possibly xenates. As members of what is Group VIII of the periodic classification, Xe and Rn ought to have even-numbered valence states, and the established simple fluorides obey this rule. Presumably both Xe^+ and Xe^{2+} are paramagnetic ions.

63-6. Bartlett, Neil

UNUSUAL OXIDATION STATES OF THE NOBLE ELEMENTS, Chemistry in Canada **15**, 33-40 (1963).

A brief review of the higher-oxidation-state fluorides and oxide fluorides of the transition metals is followed

by details of the preparation of the first noble gas compounds. Projections are made, based on average bond-energy calculations, of the relative stabilities of some noble gas fluorides, oxides, and chlorides.

63-7. Bartlett, Neil, and N. K. Jha

THE XENON-PLATINUM HEXAFLUORIDE REACTION AND RELATED REACTIONS, pp. 23-30 of "Noble-Gas Compounds," Chicago, Univ. of Chicago Press, 1963.

Xenon and platinum hexafluoride interact at room temperature to form a red solid of composition $\text{Xe}(\text{PtF}_6)_x$, where x lies between 1 and 2. That the platinum is present in the +5 oxidation state, no matter what the composition of the adduct, is indicated by the preparation of alkali metal hexafluoroplatinates(V) from material of composition XePtF_6 and $\text{Xe}(\text{PtF}_6)_2$. Material containing more than one mole of platinum hexafluoride per gram atom of xenon combines with more xenon at 130°C to approach the composition XePtF_6 . Xenon tetrafluoride is liberated in the pyrolysis of platinum hexafluoride-rich adduct, $\text{Xe}(\text{PtF}_6)_{1.8}$. The residual, brick-red, diamagnetic, xenon-containing platinum compound has a composition close to $\text{XePt}_2\text{F}_{10}$. Rhodium hexafluoride forms a deep-red adduct with xenon, the composition of which is close to XeRhF_6 . Krypton does not react with either platinum hexafluoride or with rhodium hexafluoride at temperatures below 50°C.

63-8. Bartlett, N., and R. R. Rao

XENON HYDROXIDE: AN EXPERIMENTAL HAZARD, Science **139**, 506 (1963).

A 0.39-g sample of xenon tetrafluoride dissolved in 1.5 ml of distilled water reacted vigorously and left a white solid. The solid detonated when warmed under vacuum above 30 or 40°C and completely shattered the enclosing vessel.

63-9. Bersohn, Richard

BONDING WAVEFUNCTIONS IN THE XENON FLUORIDES, J. Chem. Phys. **38**, 2913-14 (1963).

A quadrupole coupling criterion is proposed to evaluate the bonding in the xenon fluorides. Localized valence bonds will give a much higher quadrupole coupling constant for ^{131}Xe than the delocalized linear combination of p functions used in the polyhalides.

63-10. Bhatnagar, Vijay Mohan

CLATHRATE COMPOUNDS OF QUINOL, Def. Sci. J. (N. Delhi), Suppl. **13**(4), 57-66 (1963).

A clathrate is a single-phase solid consisting of a host and the guest; the guest is retained in closed cavities provided by the crystal lattice of the host. H bonding between the OH groups of quinol molecules results in a lattice which enmeshes several volatile compounds, such as H_2S , SO_2 , and the halogens, to form stable crystal complexes (Powell, CA 45, 18a). The preparation and physicochemical properties of quinol clathrates(I) and the structural characteristics influencing formation of I are reviewed. I of rare gases are granular compounds. ^{133}Xe and ^{85}Kr , which are by-products of nuclear fission, can be conveniently stored and handled as I and thus prevented from polluting the atmosphere. The gaseous component of I is ~10% of the total weight and can be easily released by heat.

Quinol- ^{85}Kr clathrate produces 25 times more intense radiation and is an ideal source of β -radiation for thickness measurements. ^{133}Xe emits γ rays of 81 keV, and as I is a compact radiographic source for specific applications. Several other applications are described. 77 References.

63-11. Blinc, R., P. Podnar, J. Slivnik, and B. Volavšek

A ^{19}F MAGNETIC RESONANCE STUDY IN XENON TETRAFLUORIDE, Phys. Letters **4**, 124 (1963).

Magnetic-resonance chemical shifts and second moments of ^{19}F were measured in polycrystalline XeF_4 as a function of temperature and magnetic field to obtain information on the electronic structure and the dynamics and distribution of fluorine atoms in XeF_4 .

63-12. Blinc, R., P. Podnar, J. Slivnik, B. Volavšek, S. Maričić, and Z. Vekslj

ANISOTROPY OF FLUORINE CHEMICAL SHIFT IN SOLID XENON TETRAFLUORIDE, pp. 270-4 in "Noble-Gas Compounds," H. H. Hyman, ed., Chicago, University of Chicago Press, 1963.

The fluorine chemical shift for XeF_4 (448 ppm for F_2) probably supports the postulate of substantial ionic character for the XeF bond. Similarly, the anisotropy of the chemical-shift tensor must be interpreted in terms of a contribution to chemical bonding beyond a single covalent bond.

63-13. Blinc, R., I. Zupančič, S. Maričić, and Z. Vekslj

ANISOTROPY OF THE FLUORINE CHEMICAL SHIFT TENSOR IN XENON TETRAFLUORIDE, J. Chem. Phys. **39**, 2109-10 (1963).

Shift anisotropy in XeF_4 was investigated, and attempts were made to determine the differences between the principal values of the ^{19}F shift tensor in XeF_4 as precisely as possible. In all cases studied the line shape was sufficiently close to that expected for this case of axial symmetry of the shift tensor so that the second moment method could be used to determine the shift anisotropy. The difference in the principal values of the shift tensor was determined to be $\Delta\sigma = 5.7 \times 10^{-4}$. From the results it was concluded that the Xe-F distance at -100°C should be a little bit shorter than previously suggested by room-temperature diffraction data.

63-14. Bohn, R. K., K. Katada, J. V. Martinez, and S. H. Bauer

AN ELECTRON-DIFFRACTION STUDY OF THE STRUCTURE OF GASEOUS XENON TETRAFLUORIDE, pp. 238-42 of "Noble-Gas Compounds," Chicago, Univ. of Chicago Press, 1963.

The structure of gaseous XeF_4 was determined by electron diffraction. The radial-distribution curve shows a principal peak at 1.94 Å, corresponding to the Xe-F distance. The peak yields a root-mean-square amplitude of vibration of approximately 0.05 Å. In addition, the radial-distribution curve shows two other maxima at 2.77 and 3.88 Å. The peak at 3.88 Å is approximately 1/3 that of the one at 2.77 Å. Approximating the peak at 2.77 Å with a gaussian curve yields a root-mean-square amplitude of vibration of 0.10 Å. The results

show that gaseous xenon tetrafluoride is square planar to within experimental error.

63-15. Boudreaux, Edward A.

A SEMI-EMPIRICAL MO TREATMENT OF THE ELECTRONIC STRUCTURE OF XENON HEXAFLUORIDE, pp. 354-7 of "Noble-Gas Compounds," Chicago, Univ. of Chicago Press, 1963.

The electronic structure of XeF_6 is treated according to the Wolfsberg-Helmholz procedure in an attempt to find a reasonable scheme for the electronic distribution and to identify the lowest electronic excited state.

63-16. Brocklehurst, B.

LIGHT EMISSION FROM GASES IRRADIATED WITH X RAYS, (AERE-C/R-2669) (Dec 1963), 73p.

The emission spectra between 2000 and 7000 Å excited in gases by X rays have been photographed, and the intensities of individual bands measured with a photomultiplier at pressures between 1 and 700 mm. The long range of the secondary electrons gives a complicated energy-absorption characteristic. Carbon dioxide shows emission from CO_2^+ , while nitrogen gives the first negative (N_2^+) and second position (N_2) band systems. The change in vibrational temperature with pressure has been studied in the latter system. Nitrous oxide emits the β bands of nitric oxide and some previously unknown bands which are ascribed to N_2O^+ . Nitric oxide, alone and in mixtures, gives a very feeble emission, probably due to the chemiluminescent reaction $\text{NO} + \text{O} \rightarrow \text{NO}_2 + \text{hv}$. The inert gases show a remarkable change from line spectra only, in neon, to continua in xenon; added gases are readily excited by the long-lived metastable states of the inert gases.

73 References.

63-17. Brown, T. H., E. B. Whipple, and P. H. Verdier
HIGH RESOLUTION ^{19}F and ^{129}Xe MAGNETIC DOUBLE
RESONANCE SPECTRUM OF XeOF_4 , J. Chem. Phys.
38, 3029-30 (1963).

Double resonance experiments were carried out by observing the ^{19}F resonances at 56.442 Mc/sec while injecting a "tickling" frequency in the vicinity of 16.7 Mc/sec across the transmitter coil of the spectrometer probe. A nominal chemical shift for ^{129}Xe of 5511 ppm downfield from atomic xenon is found after correcting for the shift of the HF reference. The corresponding shift for ^{129}Xe in XeF_4 is 5785 ppm.

63-18. Brown, Thomas H., E. B. Whipple, and
Peter H. Verdier

HIGH-RESOLUTION MAGNETIC RESONANCE OF
XENON COMPOUNDS, pp. 263-9 of "Noble-Gas
Compounds," Chicago, Univ. of Chicago Press, 1963.

Studies were made of the magnetic-resonance spectra of XeF_2 , XeF_4 , XeOF_4 , and XeF_6 dissolved in anhydrous HF. At room temperature, solutions of XeF_4 and XeOF_4 show resolved fluorine spectra, whereas those of XeF_2 and XeF_6 show a single fluorine resonance, indicating chemical exchange with the solvent. On cooling, a resolved fluorine spectrum is obtained from XeF_2 . The resolved fluorine spectra all consist of symmetrical three-line patterns plus the strong solvent line, illustrated by the XeF_2 spectrum at 56.442 Mc. Qualitatively similar spectra are obtained

at 15.000 Mc. Separation of the weak outer lines is found to be independent of the magnetic field, while the separation of the center of the three-line pattern from the H^{19}F resonance is proportional to magnetic field. Application of a second radiofrequency field at one of the ^{129}Xe resonance frequencies perturbs the satellite ^{19}F lines, demonstrating conclusively that they result from the bonding of fluorine to ^{129}Xe .

63-19. Brown, Thomas H., E. B. Whipple, and
P. H. Verdier

XENON TETRAFLUORIDE: FLUORINE-19 HIGH-
RESOLUTION MAGNETIC RESONANCE SPECTRUM,
Science 140, 178 (1963).

The ^{19}F spectrum of XeF_4 dissolved in anhydrous HF was observed at two frequencies, yielding a ^{19}F chemical shift of 175 ppm to lower field than the solvent and a ^{129}Xe - ^{19}F spin-spin coupling constant, confirmed by double irradiation, of 3860 cps. Absence of fast ^{19}F chemical exchange and collapse of the ^{131}Xe - ^{19}F coupling by quadrupole relaxation may be inferred from the spectrum.

63-20. Burns, John H.

A SECOND CRYSTALLINE PHASE OF XENON
TETRAFLUORIDE, J. Phys. Chem. 67, 536 (1963).

A second modification of XeF_4 was prepared by condensation from the vapor near room temperature. This modification is less stable and has a greater density than the first phase. The unit-cell dimensions are: $a = 6.64 \pm 0.01$ Å, $b = 7.33 \pm 0.01$ Å, $c = 6.40 \pm 0.01$ Å, and $\beta = 92^\circ 40' 5''$; the probable space group is $P2_1/c$.

63-21. Burns, John H., Paul A. Agron, and
Henri A. Levy

THE CRYSTAL AND MOLECULAR STRUCTURE OF
XENON TETRAFLUORIDE BY NEUTRON
DIFFRACTION, pp. 211-20 of "Noble-Gas Compounds,"
Chicago, Univ. of Chicago Press, 1963.

The crystal structure, molecular geometry, and thermal motion of XeF_4 were determined by three-dimensional neutron-diffraction analysis. The symmetry of the XeF_4 molecule was found to be D_{4h} to high precision. The average Xe-F bond length, corrected for thermal motion, is 1.95 ($\sigma = 0.01$) Å, and the $\text{F}(1)$ -Xe-F(2) angle is 90.0 ($\sigma = 0.1$)°. Thermal motion in the crystal is described as a translation of the rigid molecule plus a libration of approximately 5° about the three molecular axes. Each fluorine atom makes eight intermolecular contacts with other fluorine atoms and one close approach to another xenon atom.

63-22. Burns, John H., P. A. Agron, and H. A. Levy

XENON TETRAFLUORIDE MOLECULE AND ITS
THERMAL MOTION: A NEUTRON DIFFRACTION
STUDY, Science 139, 1208-9 (1963).

A neutron-diffraction analysis of the XeF_4 crystal structure confirmed the square-planar symmetry of the molecule. From the data, the average Xe to F bond length is 1.953 Å ($\sigma = 0.002$), and the F to Xe to F angle is 90.0° ($\sigma = 0.1$). A description of the thermal displacements in the crystal is given.

63-23. Burns, John H., R. D. Ellison, and H. A. Levy
THE CRYSTAL STRUCTURE OF THE MOLECULAR
ADDITION COMPOUND XENON DIFLUORIDE-XENON
TETRAFLUORIDE, *J. Phys. Chem.* **67**, 1569-70 (1963).

Diffraction intensities from a single crystal of $\text{XeF}_2 \cdot \text{XeF}_4$ were measured, and a total of 574 independent reflections was recorded, which included virtually all having detectable intensity. The approximate shape of the crystal was determined, making it possible to calculate an absorption correction for each reflection. The mean diameter of the crystal was about 0.015 cm; the value of the absorption coefficient used was 119.5 cm^{-1} . A trial structure (and the formula) was determined by the Fourier synthesis method. Molecular patterns were also found for the crystal. The hypothesis that the XeF_4 molecule is square-planar was found to be consistent with the study, and the individual molecular geometries are retained in the compound with very little change. There also was no structural evidence for the formation of any strong bonds between molecules, and the phase appears to be appropriately described as a molecular addition compound.

63-24. Burns, John H., R. D. Ellison, and
Henri A. Levy

THE CRYSTAL STRUCTURE OF $\text{XeF}_2 \cdot \text{XeF}_4$ BY X-RAY
DIFFRACTION, pp. 226-8 of "Noble-Gas Compounds,"
Chicago, Univ. of Chicago Press, 1963.

A previously described xenon fluoride called the high-density form of XeF_4 was determined by crystal structure to be a new compound $\text{XeF}_2 \cdot \text{XeF}_4$. The crystal data were found to be $a = 6.64$, $b = 7.33$, and $c = 6.40 \text{ \AA}$, $\beta = 92^\circ 40'$, the probable space group, $P2_1/c$, and the arrangement of Xe atoms as a face-centered array. Two XeF_2 molecules were found to be centered in positions 2(a): 0, 0, 0; 0, 1/2, 1/2, and two XeF_4 molecules centered in positions 2(d): 1/2, 0, 1/2, 1/2, 1/2, 0. Intermolecular fluorine-to-xenon contacts of 3.28, 3.35, 3.35, 3.37, and 3.42 \AA were found in $\text{XeF}_2 \cdot \text{XeF}_4$. Therefore, the phase is appropriately described as a molecular addition compound.

63-25. Chernick, Cedric L.

FLUORIDES OF XENON, PREPARATION AND
PROPERTIES. AN INTRODUCTION AND REVIEW.,
pp. 35-8 in "Noble-Gas Compounds," H. H. Hyman, ed.,
Chicago, University of Chicago Press, 1963.

Preparation and properties summarized as known at
the time of the Argonne symposium.

63-26. Chernick, Cedric L.

THE IGNOBLE GASES: A CHEMICAL SOMERSAULT,
New Scientist **19**, 444-6 (1963).

Work in preparing compounds of rare gases is discussed. Reactions of xenon with platinum hexafluoride, ruthenium hexafluoride, and fluorine, as well as a controlled hydrolysis of XeF_4 to produce XeO_3 , XeOF_4 , and a sodium perxenatate are described. Properties of the compounds are listed. Radon and krypton fluorides were also prepared. Possible uses for compounds of the rare gases are discussed.

63-27. Chernick, Cedric L., H. H. Claassen,
John G. Malm, and P. L. Plurien

XENON OXYTETRAFLUORIDE, p. 106-8 of "Noble-
Gas Compounds," Chicago, Univ. of Chicago Press,
1963.

Xenon oxytetrafluoride, XeOF_4 , was prepared by the reaction of XeF_4 with water or silica. The compound is a colorless liquid with a melting point of -28°C and a vapor pressure of 8 mm at 0°C .

63-28. Chernick, Cedric L.

CHEMICAL COMPOUNDS OF THE NOBLE GASES,
Record Chem. Progr. **24**, 139-55 (1963).

A historical review is presented of the prediction and discovery of compounds of Kr, Xe, and Rn. The many attempts to prepare the compounds are described. The properties and structure of Xe compounds are discussed in detail. A bibliography of 123 references is included.

63-29. Chernick, C. L., C. E. Johnson, J. G. Malm,
G. J. Perlow, and M. R. Perlow

THE MÖSSBAUER EFFECT IN CHEMICAL
COMPOUNDS OF ^{129}Xe , *Phys. Letters* **5**, 103-4 (1963).

Measurements were made using the 40-keV $3/2^+ \rightarrow 1/2^+$ transition in ^{129}Xe with absorbers of XeF_2 , XeF_4 , a xenate having the nominal formula $\text{Na}_4\text{XeO}_6 \cdot \text{H}_2\text{O}$, and the hydroquinone clathrate of Xe containing 28% of Xe by weight. The clathrate and xenate show a single line unshifted from zero velocity, while the fluorides exhibit large quadrupole splittings and no net isomer shift. The lifetime of the $3/2^+$ states was determined to be $0.58 \pm 0.07 \text{ nsec}$. Evidence for a Xe valence of 8 was found in the xenate. Splitting in XeF_2 and XeF_4 was measured as $4.19 \pm 0.11 \text{ cm/sec}$.

63-30. Claassen, H. H.

RESUME ON VIBRATIONAL SPECTRA OF XENON
COMPOUNDS, pp. 304-5 of "Noble-Gas Compounds,"
Chicago, Univ. of Chicago Press, 1963.

Results of experiments on the infrared and Raman spectra of XeF_2 , XeF_4 , XeF_6 , and XeOF_4 are discussed.

63-31. Claassen, Howard H., Cedric L. Chernick, and
John G. Malm

VIBRATIONAL SPECTRA AND STRUCTURE OF
XENON TETRAFLUORIDE, *J. Am. Chem. Soc.* **85**,
1927-8 (1963).

The infrared spectrum of XeF_4 vapor has strong bands at 123, 291, and 586 cm^{-1} . The Raman spectrum of the solid has very intense peaks at 502 and 543 cm^{-1} , and weaker ones at 235 and 442 cm^{-1} . These data show that the molecule is planar and of symmetry D_{4h} . The seven fundamental frequencies were assigned as 543 (a_{1g}), 291 (a_{2u}), 235 (b_{1g}), 221 (b_{1u}), 502 (b_{2g}), 586 (e_u), and 123 (e_u). The (b_{1u}) frequency value is quite uncertain.

63-32. Claassen, H. H., Cedric L. Chernick, and John G. Malm

VIBRATIONAL SPECTRA AND STRUCTURES OF XENON TETRAFLUORIDE AND XENON OXYTETRAFLUORIDE, pp. 287-294 in "Noble-Gas Compounds," Chicago, Univ. of Chicago Press, 1963.

The infrared spectrum of XeF_4 vapor has strong bands at 123, 291, and 586 cm^{-1} . The Raman spectrum of the solid has very intense peaks at 502 and 543 cm^{-1} , and a weaker one at 235 cm^{-1} . These data show that the molecule is planar and of symmetry D_{4h} . The seven fundamental frequencies have been assigned as 543 (a_{1g}), 291 (a_{2u}), 235 (b_{1g}), 221 (b_{1u}), 502 (b_{2g}), 586 (e_u), and 123 (e_u) cm^{-1} , the assignment of 221 cm^{-1} to b_{1u} being uncertain.

The infrared spectrum of XeOF_4 vapor has intense peaks at 288, 362, 578, 609, and 928.2 cm^{-1} , and the Raman spectrum of the liquid has bands at 231, 286, 364, 530, 566, and 918 cm^{-1} . The spectra fit a C_{4v} model very well. The fundamentals determined are: 928.2 (a_1), 578 (a_1), 288 (a_1), 231 (b_1), 530 (b_2), 609 (e), and 362 (e) cm^{-1} . This leaves one (b_2) and one (e) fundamental undetermined. Very close correspondence between vibrations in the two molecules indicates that the O-Xe-F angle in XeOF_4 must be rather close to 90°.

63-33. Claassen, Howard H., and John G. Malm

COMPOUNDS OF XENON, Chemistry 36, 9-16 (1963).

A review of the work leading to the preparation of XeF_4 , and a discussion of its molecular structure.

63-34. Claassen, H. H., John G. Malm, and H. Selig

REMARKS RELATIVE TO THE FIRST XENON TETRAFLUORIDE PREPARATION, pp. 31-32 of "Noble-Gas Compounds," Chicago, Univ. of Chicago Press, 1963.

The reaction between xenon and fluorine was done quantitatively, using a thin-walled nickel can that could be weighed. From weights combined, the formula XeF_4 was arrived at, and evidence for the existence of a lower fluoride was also obtained. Visual evidence was obtained by subliming some of the material into glass. The formula was verified by chemical analysis.

63-35. Dudley, Francis B., Gary Gard, and George H. Gady

XENON HEXAFLUORIDE, Inorg. Chem. 2, 228-9 (1963); also pp. 61-63 in "Noble-Gas Compounds," Chicago, Univ. of Chicago Press, 1963.

The effects of pressure and temperature on xenon-fluorine mixtures were studied. Xe-F mixtures were introduced into a 1500-cc prefluorinated nickel vessel and the pressure-temperature dependence followed from room temperature up to 720°K. The mixtures followed ideal gas behavior up to 390°K, when a pressure decrease began to occur. The pressure decreased rather rapidly in the temperature range from 480 to 520°K until the total decrease was about 2.5 times the pressure which would have been due to xenon alone. Above 560°K the rate of increase in pressure with temperature was abnormally large, thereby suggesting the dissociation of a molecular species. At about 710°K the pressure versus temperature curve merged

into that expected for a mixture of F_2 with XeF_4 . Empirical formulas of xenon fluoride formed at 50, 150, and 25 atm were also calculated.

63-36. Dwyer, O. E., and R. H. Wiswall
CHEMISTRY AND CHEMICAL ENGINEERING DIVISION, BNL-799, pp. 26-54, 1963.

A progress report covering work on many problems. ...The irradiation of xenon-fluorine mixtures was found to produce mixtures of XeF_2 and XeF_4 . The radiolysis of two more fluorocarbons, the analogues of cyclohexane and bicyclohexyl, was investigated. ...

63-37. Edwards, A. J., J. H. Holloway, and R. D. Peacock

SOME PROPERTIES OF THE XENON FLUORIDES, pp. 71-2 of "Noble-Gas Compounds," Chicago, Univ. of Chicago Press, 1963.

Chemical properties of XeF_4 are reported and discussed. The properties, which are incomplete, show that the XeF_4 is a poorer Lewis acid than iodine pentafluoride and that it is a Lewis base only under special conditions. A lack of reactivity of XeF_4 towards BF_3 suggests that π -bonding plays an important part in complex formation.

63-38. Edwards, A. J., J. H. Holloway, and R. D. Peacock

NEW FLUORINE COMPOUNDS OF XENON, Proc. Chem. Soc. 275 (1963).

XeF_4 dissolves in liquid SbF_5 to give a solution from which a yellow, diamagnetic solid (m.p. 63°C) can be isolated. This complex, $\text{XeF}_2 \cdot 2\text{SbF}_5$ can just be sublimed under vacuum at 60°C, distills unchanged at -120°C under vacuum, and is stable at even higher temperatures. The compound can also be made from XeF_2 and SbF_5 .

XeF_4 and TaF_5 yield a similar complex, $\text{XeF}_2 \cdot 2\text{TaF}_5$ (m.p. 81°C).

XeF_4 does not react with BF_3 at temperatures up to 200°C, nor does it react with NaF or KF.

63-39. Falconer, W. E., and J. R. Morton

RADIATION DAMAGE IN XENON TETRAFLUORIDE, ELECTRON SPIN RESONANCE OF THE TRAPPED RADICAL XeF_3 , pp. 245-50 of "Noble-Gas Compounds," Chicago, Univ. of Chicago Press, 1963.

On γ irradiation of XeF_4 at 77°K the radical XeF_3 is trapped in the crystal lattice. The electron-spin resonance spectrum of XeF_3 was interpreted, and it appears that the unpaired electron occupies an antibonding σ orbital of predominantly fluorine 2p- and xenon 5p-character.

63-40. Falconer, W. E., and J. R. Morton

ELECTRON SPIN RESONANCE SPECTRUM OF THE XeF_3 RADICAL, Proc. Chem. Soc., 95-6 (1963).

A single crystal of XeF_4 was irradiated at 77°K with 5 Mrad of ^{60}Co γ rays, and its paramagnetic resonance spectrum was studied at 77°K. The spectrum is attributed to the species XeF_3 and is consistent with the known isotopic distribution in xenon. The isotropy of

the spectra implies that the Xe-F bond is probably parallel to the longitudinal axis of the crystal. Approximate hyperfine splittings for ^{19}F , ^{129}Xe , and ^{131}Xe are 180, 425, and 125 G, respectively.

63-41. Fields, P. R., L. Stein, and M. H. Zirin

RADON FLUORIDE: FURTHER TRACER EXPERIMENTS WITH RADON, pp. 113-9 in "Noble-Gas Compounds," Chicago, Univ. of Chicago Press, 1963.

It has been shown in tracer experiments that radon fluoride can be prepared by heating mixtures of radon and fluorine to 400°C. The compound is very stable and distills at 230 to 250°C at a pressure of approximately 10^{-6} mm Hg. It can be reduced with hydrogen at 500°C to recover elemental radon.

Attempts to prepare a radon chloride by thermal and photochemical methods have been unsuccessful thus far. No chemical reactions have been detected in mixtures of radon and oxygen irradiated with ultraviolet light or passed through a Berthelot-type ozone generator. However, it has been observed that the high-voltage electrical discharge used to produce ozone causes some radon to be strongly fixed on Pyrex surfaces. Microwave discharges have also been found to be very effective in fixing radon on quartz and Pyrex. In experiments with a metal microwave cell, radon has been fixed on a central brass antenna and subsequently released by heating the brass to the softening point ($\sim 900^\circ\text{C}$).

63-42. Finkel, A. J., C. E. Miller, and J. J. Katz

METABOLIC AND TOXICOLOGIC STUDIES OF WATER-SOLUBLE XENON COMPOUNDS, pp. 309-14 in "Noble-Gas Compounds," Chicago, Univ. of Chicago Press, 1963.

Some observations have been made of the metabolic and toxicologic effects in mice of injections of aqueous solutions of sodium xenate. Sodium xenate has been found to be moderately toxic when injected intravenously, and the median lethal dose lies between 15 and 40 mg/kg. The administered sodium xenate appears to be rapidly reduced to xenon gas, and by the use of radio xenon and sensitive detection equipment, it has been shown that the bulk of the xenon gas leaves the body within minutes after injection.

63-43. Gard, Gary L., Francis B. Dudley, and George H. Cady

REACTIONS OF XENON WITH CERTAIN STRONG OXIDIZING AGENTS, pp. 109-12 in "Noble-Gas Compounds," H. H. Hyman, ed., Chicago, University of Chicago Press, 1963.

Xenon may be fluorinated to the difluorides by oxygen difluoride (OF_2), trifluoromethyl hypofluorite (CF_3OF), and fluorine fluorosulfate (FSO_3F), though not by peroxodisulfuryl difluoride ($\text{FSO}_3)_2$.

63-44. Gillespie, R. J.

THE NOBLE-GAS FLUORIDES, OXYFLUORIDES, AND OXIDES PREDICTIONS OF MOLECULAR SHAPES AND BOND LENGTHS, pp. 333-9 of "Noble-Gas Compounds," Chicago, Univ. of Chicago Press, 1963.

It is shown how the shapes of known and as yet unknown rare gas compounds may be predicted and how, by comparison with the interhalogen compounds, the bond lengths in the molecules may also be estimated. The basic assumption of the theory is that the bonds in the molecules are essentially localized electron-pair bonds whose arrangement in space is determined by the mutual interactions of all the electron pairs in the valence shell of the central atom. Lone pairs exert greater repulsions than single-bond pairs, and oxygen atoms are assumed to be bonded by double bonds containing two electron pairs, which also exert greater repulsions than single-bond electron pairs.

63-45. Grosse, A. V., A. D. Kirshenbaum, A. G. Streng, and L. V. Streng

KRYPTON TETRAFLUORIDE: PREPARATION AND SOME PROPERTIES, Science **139**, 1047-8 (1963).

Kr and F_2 do not react at high temperatures. However, KrF_4 was prepared by electric discharge at low temperatures, using a vessel with copper electrodes. In one experiment, 500 cm^3 of a 1:2 mixture of Kr and F_2 were completely converted to 1.15 g KrF_4 in 4.0 hr; the KrF_4 is deposited on the glass wall of the discharge vessel in the form of a white solid. KrF_4 is much less thermally stable than XeF_4 , but it can be stored for weeks at -78°C without decomposing. The vapor pressure, corrected for decomposition, was measured and found to follow the equation $\log_{10} p(\text{mm}) = 8.531 - (1930/T)$; $\Delta H_{\text{subl}} = 8840 \pm 300$ cal/mole, and extrapolated sublimation temperature $\approx 70^\circ\text{C}$.

63-46. Gruen, Dieter M.

INFRARED ABSORPTION SPECTRA OF SOME HEAVY METAL PERXENATES, pp. 174-80 in "Noble-Gas Compounds," H. H. Hyman, ed., Chicago, University of Chicago Press, 1963.

Perxenates have an absorption band in the 650-680 cm^{-1} region. Analogy with paraperiodic acid, tellurates, and antimonates suggests that this band is associated with the $\nu_2(\text{f}_{1u})$ vibration in an octahedral XeO_6 grouping. Silver perxenate is the least thermally stable of available salts, including alkali and alkaline earth members, copper, silver, lead, and uranyl salts.

63-47. Gunn, Stuart R.

THE HEAT OF FORMATION OF XENON TRIOXIDE, pp. 149-151 of "Noble-Gas Compounds," H. H. Hyman, ed., Chicago, University of Chicago Press, 1963.

The heat of explosion of XeO_3 was measured calorimetrically; the derived heat of formation is $+96 \pm 2$ kcal/mole.

63-48. Gunn, Stuart R., and Stanley M. Williamson

THE HEAT OF FORMATION OF XENON TETRAFLUORIDE, pp. 133-8 in "Noble-Gas Compounds," Chicago, Univ. of Chicago Press, 1963.

The heat of reaction of XeF_4 with aqueous iodide solution has been measured. The standard heat of formation of the solid is $-60 \text{ kcal mole}^{-1}$, and the average thermochemical bond energy is 30 kcal.

63-49. Gunn, Stuart R., and Stanley M. Williamson

XENON TETRAFLUORIDE: HEAT OF FORMATION, Science **140**, 177-8 (1963).

Calorimetric measurements of the heat of reaction of XeF_4 with aqueous iodide solution give -60 kcal/mole for the standard heat of formation, or an average thermochemical bond energy of about 31 kcal.

63-50. Hamilton, Walter C., and James A. Ibers

X-RAY INVESTIGATION OF THE CRYSTAL STRUCTURE OF XENON TETRAFLUORIDE, pp. 195-202 of "Noble-Gas Compounds," Chicago, Univ. of Chicago Press, 1963.

The crystal structure of XeF_4 , reported earlier by us, has been refined further. The average Xe-F bond length, uncorrected for thermal motion, is $1.94 \pm 0.02 \text{ \AA}$. The F-Xe-F bond angle is $90.8 \pm 1.1^\circ$. As the molecule is required by the space-group symmetry to be planar and centrosymmetric, these results indicate that any departures from a square-planar configuration for the molecule are insignificant. The thermal vibrations of the molecule, as derived from the anisotropic thermal parameters, are readily interpreted in terms of rigid-body translations and rotations with root-mean-square amplitudes of approximately 0.12 \AA and 6° , respectively. The latter correspond to torsional oscillations with frequencies of about 50 to 70 cm^{-1} .

63-51. Hamilton, W. C., J. A. Ibers, and

D. R. MacKenzie

GEOMETRY OF THE PERXENATE ION, Science **141**, 532 (1963).

Reaction of XeF_4 with NaOH yields colorless crystals containing octavalent xenon. A three-dimensional X-ray analysis indicates these crystals to be sodium perxenate octahydrate, $\text{Na}_4\text{XeO}_6 \cdot 8\text{H}_2\text{O}$. The measured density of this compound, $2.33 \pm 0.05 \text{ g cm}^{-3}$, is in good agreement with the X-ray density of 2.38 g cm^{-3} , calculated assuming eight water molecules in the unit cell. The XeO_6^{4-} ion has an approximately octahedral configuration with the mean Xe-O bond lengths being $1.875 \pm 0.021 \text{ \AA}$. This is 0.12 \AA longer than Xe-O in XeO_3 , a difference which is compatible with the difference of 0.13 \AA in the isoelectronic iodine-oxygen compounds.

63-52. Haubach, W. J., C. F. Eck, W. M. Rutherford, and W. L. Taylor

STATUS OF STABLE GASEOUS ISOTOPE SEPARATION AND PURIFICATION AT MOUND LABORATORY - 1963, MLM-1239 (Dec. 31, 1963).

An account is given of work which was carried out in 1963 in the investigative program on isotope

separation. The work includes carbon isotope separation; helium-3 separation; purification, and research; neon isotope separation; argon isotope separation; krypton isotope separation; xenon isotope separation and purification; and thermal diffusion research.

63-53. Hemmerich, P.

STRUCTURE AND THEORETICAL SIGNIFICANCE OF NOBLE GAS COMPOUNDS, Chimia **17**, 289-92 (1963). (In German.)

Reactions of rare gases with fluorine, the structures of the compounds formed, and their significance in the theory of the nature of chemical bonds are discussed.

63-54. Hiebert, Erwin N.

HISTORICAL REMARKS ON THE DISCOVERY OF ARGON, THE FIRST NOBLE GAS, pp. 3-20 of "Noble-Gas Compounds," Chicago, Univ. of Chicago Press, 1963.

A review on the discovery of argon is presented.

63-55. Hindman, J. C., and A. Svirnickas

NUCLEAR MAGNETIC RESONANCE STUDIES OF XENON FLUORIDES, pp. 251-62 of "Noble-Gas Compounds," Chicago, Univ. of Chicago Press, 1963.

Shielding values of 310, 482, and 612 ppm relative to gaseous fluorine were measured for the solid xenon hexafluoride, tetrafluoride, and difluoride, respectively. The shielding of XeF_4 shows little change in going from the vapor to the solid phase. XeF_4O , with a shielding constant of 326 ppm in the liquid phase, shows a doublet structure due to ^{129}Xe - ^{19}F coupling. The coupling constant is 1086 cps. In hydrofluoric acid, XeF_4 undergoes exchange with the solvent. XeF_4 appears to dissolve without appreciable reaction with the solvent. A ^{129}Xe - ^{19}F coupling constant of 3860 cps is found for this compound in HF media. Although XeF_4 undergoes exchange with the solvent at room temperature, the rate is sufficiently decreased on lowering the temperature to allow measurement of the ^{129}Xe - ^{19}F coupling. The observed coupling constant is 5600 cps. Failure to observe any ^{131}Xe - ^{19}F coupling is consistent with the molecular symmetries of the solid compounds. The interpretation of the shielding data in terms of electron densities on the fluorine is discussed. Possible interpretations of the coupling constants in terms of bond configurations are also considered.

63-56. Hinze, Juergen, and Kenneth S. Pitzer

IONIC OR D-HYBRID BONDS IN NOBLE-GAS HALIDES, pp. 340-6 of "Noble-Gas Compounds," Chicago, Univ. of Chicago Press, 1963.

Discussion is presented on bonding in rare gas halides: one theory describes the bonds as covalent involving d hybrids, while the other describes them as half ionic without d hybridization. The results of computations show that the principal contribution to the bonding arises from ionic character and not from d hybridization. However, it is pointed out that large changes in the numbers, ionic and d contribution, may result if different approximations are used in the calculations. In similar computations, not including overlap, the ionic contributions were found to be lower by approximately 1/4, while a d contribution twice as large was

obtained. On the other hand, the average dissociation energies varied little in different calculations. In both computations the fluorides of argon and neon as well as the chlorides or bromides of all inert gases appeared unstable.

63-57. Hoppe, Rudolf, Harald Mattauch, Karl Martin Roedder, and Wolfgang Dähne

ON THE FLUORINATION OF XENON: XENON DIFLUORIDE, pp. 98-100 of "Noble-Gas Compounds," Chicago, Univ. of Chicago Press, 1963.

A method is described for the preparation of XeF_2 by electric discharge using an induction coil. Pure XeF_2 was obtained.

63-58. Hoppe, R., H. Mattauch, R. M. Roedder, and W. Dähne

XENON DIFLUORIDE, XeF_2 , Z. Anorg. Allgem. Chem. 324, 214-24 (1963). (In German.)

By subjection to discharges from an induction coil, mixtures of xenon and fluorine yielded xenon difluoride, XeF_2 , which condensed on a cool finger (-78°C). XeF_2 is colorless, has a characteristically nauseating odor, shows birefringence, is diamagnetic, and sublimes without decomposition.

63-59. Hyman, Herbert H., ed.

NOBLE-GAS COMPOUNDS, Chicago, University of Chicago Press, 1963, 414p.

Fifty-eight articles are included.

63-60. Hyman, H. H.

NOBLE GAS COMPOUNDS, Science 141, 61 (1963).

A brief review of a meeting at Argonne National Laboratory, April 1963. The papers presented formed the basis for the book "Noble-Gas Compounds" (see 63-59).

63-61. Hyman, H. H., and L. A. Quarterman

HYDROGEN FLUORIDE SOLUTIONS CONTAINING XENON DIFLUORIDE, XENON TETRAFLUORIDE, AND XENON HEXAFLUORIDE, pp. 275-8 of "Noble-Gas Compounds," Chicago, Univ. of Chicago Press, 1963.

Xenon difluoride and hexafluoride were found to be very soluble at room temperature in anhydrous hydrogen fluoride, while xenon tetrafluoride is only sparingly soluble. Xenon difluoride appears to undergo no reaction or ionization solution. Xenon hexafluoride, on the other hand, is very soluble in anhydrous hydrogen fluoride; furthermore, the solutions are electrically conducting. Solutions containing XeF_6 are yellow liquids, comparable in color to liquid XeF_2 . The color disappears on cooling.

63-62. Ibers, J. A., and W. C. Hamilton

XENON TETRAFLUORIDE: CRYSTAL STRUCTURE, Science 139, 106-7 (1963).

X-ray analysis shows XeF_4 to be planar in the solid state, and to have approximately D_{4h} symmetry. The crystal is monoclinic with $a = 5.03 \pm 0.03$, $b = 5.90 \pm 0.03$, and $c = 5.75 \pm 0.03$ Å; $\beta = 100 \pm 1^\circ$. The space

group is probably $C_{2h}^5 - P2_1/n$. The F-Xe-F angle is $86 \pm 3^\circ$, and the Xe-F bond length is 1.92 ± 0.03 Å. The calculated density is 4.10 g cm^{-3} .

63-63.

RESEARCH LABORATORIES SEMI-ANNUAL REPORT FOR THE PERIOD JULY-DECEMBER 1963, IA-920 (Israel Atomic Energy Commission, Yavne, Soreq Research Establishment), 196p.

Progress and trends in the research program are reported, and operational services are described. Information is included on operation of the IRR-1 Reactor and isotope production. Research progress is reported on elementary-particle theory, reactor physics, nuclear physics, solid-state physics, inorganic chemistry, radiation chemistry, nuclear chemistry, analytical chemistry, and applications technology. Biological and medical research are summarized. Results of research on nuclear hazards are presented, along with research progress on nuclear and mechanical instrumentation. A bibliography of reports and papers associated with the project is included.

63-64. Israël, Yigal Julius

THE PROBLEM OF CHEMICAL BONDS IN XENON TETRAFLUORIDE, Bull. Soc. Chim. France 6, 1336 (1963). (In French.)

An electron energy-level scheme is proposed to explain the chemical properties of XeF_4 , which has the planar crystal structure D_{4h} .

63-65. Johnston, W. V., D. Pilipovich, and D. E. Sheehan

THE HEAT CAPACITY AND RELATED THERMODYNAMIC FUNCTIONS OF XENON TETRAFLUORIDE, pp. 139-43 of "Noble-Gas Compounds," Chicago, Univ. of Chicago Press, 1963.

Measurements of the heat capacity and specific heat of XeF_4 at 20°K to room temperature are reported. The entropy of XeF_4 from 0 to 298.16°K was determined from the heat capacities. The entropy of formation and free energy of formation of XeF_4 at 25°C were found to be $-102.5 \text{ cal mole}^{-1} \text{ deg}^{-1}$ and $-29.4 \text{ kcal mole}^{-1}$, respectively.

63-66. Jortner, Joshua, Stuart A. Rice, and E. Guy Wilson

SPECULATION CONCERNING THE NATURE OF BINDING IN XENON FLUORINE COMPOUNDS, J. Chem. Phys. 38, 2302-3 (1963).

A description is proposed for the bonding in XeF_2 in terms of delocalized molecular orbitals formed by combination of $p\sigma$ -type Xe and F orbitals. The energy levels and charge distribution were evaluated, and it is concluded that (1) the bond energy per XeF bond in linear XeF_2 is of the order of 4 eV for an assumed bond length of 2 Å; (2) the first allowed optical transition is $\psi(a_{1g}) \rightarrow \psi(a_{1g}')$, with a transition energy of 8.2 eV; (3) the bond energy in the XeF radical is less than the bond energy per bond in XeF_2 ; (4) the bent XeF_2 structure is less stable than the linear structure; (5) when the effects of π binding are introduced, the binding energy in XeF_2 is at a maximum at $R_{\text{Xe-F}} = 1.85$ Å. Conclusions (3), (4), and (5) are consistent

with the experimental data. It is also concluded that the migration of negative charge from Xe to F is substantial (0.5 charge unit per F atom), and indeed the behavior of XeF_2 is similar to that of ionic compounds.

63-67. Jortner, Joshua, E. Guy Wilson, and Stuart A. Rice

THE HEATS OF SUBLIMATION OF XeF_2 AND XeF_4 AND A CONJECTURE ON BONDING IN THE SOLIDS, *J. Am. Chem. Soc.* **85**, 814-15 (1963).

The heats of sublimation (ΔH_{sub}) were determined by measuring the temperature dependence of the vacuum uv absorption bands of the gas in thermal equilibrium with the crystals. A Clausius-Clayperon plot of the data gives the following values of ΔH_{sub} : XeF_2 , 12.3 ± 0.2 kcal/mole; XeF_4 , 15.3 ± 0.2 kcal/mole. The interpretation of these large ΔH_{sub} values is considered, and it is concluded that the dominant contribution to the stability of XeF_2 and XeF_4 arises from electrostatic interactions. The discrepancy in the Xe-F bond length of XeF_2 estimated from the separation of the unresolved infrared P and R branches and that calculated from X-ray data is considered briefly.

63-68. Jortner, J., E. G. Wilson, and S. A. Rice

A FAR-ULTRAVIOLET SPECTROSCOPIC STUDY OF XENON TETRAFLUORIDE, *J. Am. Chem. Soc.* **85**, 815-16 (1963).

The absorption spectrum of gaseous XeF_4 was studied in the uv region to 1100 \AA . A weak band appeared at 2265 \AA , followed by two strong bands at 1840 and 1325 \AA . Molecular orbitals relevant to the interpretation of the spectrum are given. The weak 2265-\AA band is assigned to the forbidden $a_{2u} \rightarrow e_u^\dagger$ transition. The strong 1850- and 1325-\AA bands are assigned to the allowed x, y polarized $b_{1g} \rightarrow e_u^\dagger$ and $a_{1g} \rightarrow e_u^\dagger$ transitions, respectively.

63-69. Jortner, Joshua, E. Guy Wilson, and Stuart A. Rice

THEORETICAL AND EXPERIMENTAL STUDIES OF THE ELECTRONIC STRUCTURE OF THE XENON FLUORIDES, pp. 358-90 of "Noble-Gas Compounds," Chicago, Univ. of Chicago Press, 1963.

A semi-empirical molecular-orbital model for XeF_2 and XeF_4 is presented. The results of experiments to determine the absorption spectrum in the range $1100\text{-}2500 \text{ \AA}$ and determinations of the heat of sublimation of the compounds are described. The proposed model is shown to be in good agreement with the physical and chemical properties of the compounds.

63-70. Kilpatrick, Martin

AQUEOUS SOLUTION CHEMISTRY OF XENON. AN INTRODUCTION, pp. 155-7 of "Noble-Gas Compounds," Chicago, Univ. of Chicago Press, 1963.

The hydrolysis of xenon fluorides is discussed. Hydrolysis experiments showed that in addition to the oxidation of water to oxygen there is a disproportionation of the xenon compound to higher and lower valence states for the tetra- and hexafluorides.

63-71. Kirschenbaum, A. D., and A. V. Grosse
BARIUM XENATE, *Science* **142**, 580 (1963).

Barium xenate was prepared by the addition of barium hydroxide to xenic acid. The resulting white amorphous precipitate was shown by elementary analysis to be Ba_3XeO_6 .

63-72. Kirschenbaum, A. D., L. V. Streng, A. G. Streng, and A. V. Grosse

PREPARATION OF XeF_4 (XENON TETRAFLUORIDE) BY ELECTRIC DISCHARGE, *J. Am. Chem. Soc.* **85**, 360-1 (1963).

The apparatus and conditions used in the preparation of XeF_4 by electric discharge are described. A gas mixture of 1 volume Xe and 2 volumes F_2 was used, and a quantitative yield of XeF_4 was obtained. The composition of the product was confirmed by several methods.

63-73. Koch, Charles W., and Stanley M. Williamson
THE REACTION OF AQUEOUS XENON TRIOXIDE WITH BROMIDE AND IODIDE ANION: A KINETIC STUDY, pp. 181-4 of "Noble-Gas Compounds," Chicago, Univ. of Chicago Press, 1963.

The oxidation of bromide to bromine by $\text{XeO}_3(\text{aq})$ was found to be acid dependent, and the rate in the pH range of 1 to 0 was readily measurable. Iodide was oxidized to iodine extremely rapidly at pH values < 6 , but in the region 6 to 7, rate measurements were made. Rates at 0.2 , 24.8 , and 39.9°C were observed, permitting measurement of the energies of activation for the two reactions. The appearances of Br_2^\cdot and I_2^\cdot as a function of time were observed colorimetrically on a spectrophotometer at 2650 and 2870 \AA , respectively. Consideration of the stoichiometric equation $\text{XeO}_3(\text{aq}) + 6\text{H}^+ + 9\text{X}^- \rightarrow \text{Xe} + 3\text{H}_2\text{O} + 3\text{X}_3^-$ directly gave the changes in concentrations of all species.

63-74. Lazdins, D., C. W. Kern, and M. Karplus

CHEMICAL SHIFTS IN XENON FLUORIDES, *J. Chem. Phys.* **39**, 1611-12 (1963).

The consistency of proposed bonding schemes with the chemical shifts observed in nuclear magnetic resonance studies of the XeF_n ($n = 2, 4, 6$) compounds was investigated. Equations were developed for calculating chemical shifts based on a molecular description of XeF_n compounds that postulates the formation of highly ionic bonds involving primarily the $2p$ orbitals of fluorine and the $5p$ orbitals of xenon. Comparison with experimental data showed that the molecular model is consistent with the main features of the observations.

63-75. Levy, Henri A., and P. A. Agron

THE CRYSTAL AND MOLECULAR STRUCTURE OF XENON DIFLUORIDE BY NEUTRON DIFFRACTION, *J. Am. Chem. Soc.*, **85**, 241-2 (1963); also, pp. 221-225 in "Noble-Gas Compounds," Chicago, Univ. of Chicago Press, 1963.

A neutron-diffraction study of XeF_2 at room temperature was carried out. The tetragonal body-centered lattice indicated by preliminary X-ray precession photographs was confirmed by neutron measurements of 67 nonextinguished equivalent pairs of reflections (hkl, khl) and at positions of 53 reflections required to

be absent by body centering. The symmetric linear molecules were aligned on the tetrad axes with the Xe-F distance of 1.983 ($\sigma = 0.002$) Å.

63-76. Lohr, L. L., Jr., and W. N. Lipscomb

MOLECULAR SYMMETRY OF XeF_2 AND XeF_4 , J. Am. Chem. Soc. **85**, 240-1 (1963).

The molecular structures of XeF_2 and XeF_4 were investigated in terms of a programmed semi-empirical LCAO molecular-orbital theory. Sixteen electron pairs and 17 molecular orbitals were considered for XeF_2 , with 23 electron pairs and 25 molecular orbitals for XeF_4 . Results are presented in tabular form.

63-77. Lohr, L. L., Jr., and William N. Lipscomb

AN LCAO-MO STUDY OF RARE-GAS FLUORIDES, pp. 347-53 of "Noble-Gas Compounds," Chicago, Univ. of Chicago Press, 1963.

The electronic structures of ArF_4 , KrF_4 , XeF_2 , XeF_4 , and XeF_6 are considered as a function of molecular geometry in terms of a programmed semi-empirical LCAO molecular orbital theory.

63-78. MacKenzie, D. R.

KRYPTON DIFLUORIDE: PREPARATION AND HANDLING, Science **141**, 1171 (1963).

KrF_2 was prepared by irradiation of krypton and fluorine in an electron beam (1.5 MeV) at -150°C . The compound is a white crystalline solid, stable only at temperatures below about -30°C .

63-79. MacKenzie, D. R., and R. H. Wiswall, Jr.

COMPOUND FORMATION BY GAMMA-IRRADIATION OF XENON-FLUORINE MIXTURES, Inorg. Chem. **2**, 1064 (1963).

High-intensity γ irradiation of a mixture of xenon and fluorine, in mole ratio slightly greater than 2:1 F_2 :Xe, yielded a solid which analyzed to be $\text{XeF}_{3.0}$, suggesting a mixture of XeF_2 and XeF_4 . Similar irradiations of krypton and fluorine, xenon and chlorine, and xenon and oxygen did not result in compound formation, nor did irradiation of a xenon and oxygen mixture in the Brookhaven graphite reactor.

63-80. MacKenzie, D. R., and R. H. Wiswall

THE SYNTHESIS OF XENON COMPOUNDS IN IONIZING RADIATION, pp. 81-8 in "Noble-Gas Compounds," Chicago, Univ. of Chicago Press, 1963.

Xenon and fluorine form compounds when irradiated with γ rays or energetic electrons. At and above room temperature a mixture of XeF_2 and XeF_4 is formed; at a temperature of about -35°C , XeF_2 is the only product. Utilization of absorbed energy is efficient since initial G-values for consumption of xenon are in the range from 5 to 15 atoms per 100 eV absorbed. XeF_4 is relatively stable to γ radiation, with an initial G-value of 0.6 to 1.8 at 45°C , depending on the decomposition products. Krypton and fluorine have not been made to react in an electron beam at temperatures around -130°C .

63-81. Mahieux, Francis

CHEMICAL REACTIONS BY EXPLOSION OF METAL WIRES. SYNTHESIS OF XENON HEXAFLUOROPLATINATE, Compt. Rend. **257**(5), 1083-6 (1963).

The explosion of metal wires is used to ignite gas and to set off explosives. The total chemical effect of the explosion of some metal wires in various gases is studied, especially that of Pt in a mixture of F and Xe. A sealed glass flask (of 100-ml capacity) contained the wire (of 0.10-mm diameter and 25 cm long) to be exploded, soldered between 2 Pt or W electrodes. The wire was coiled to reduce the distance between the electrodes. The 2 electrodes passed through the glass along 2 W rods in a cap on the flask. The desired gas was placed in the flask at atmospheric pressure, and the pressure was reduced. The wire was exploded by the discharge of 2 condensers mounted in parallel (16- μF total capacity) charged with a continuous potential of 2000 V. The discharge caused the incandescent wire to be dispersed in fine droplets. Whether or not there was reaction depended on the nature of the metal and of the gas, the geometric conditions in the flask, the quantity of gas, the distances traveled by the metal droplets, the cooling of the metal, and the conditions of the discharge. No reaction was observed with Cu, Au, Pt, and Al in air, with Al and Ni in CO, with Al, Mo, and W in N, or with Pt in Alzone (a commercial mixture containing O, CFCl_3 , CCl_2F_2 , and 10 vol % O_2). Reaction occurred with Ni, Ag, and Al in Alzone, with Mn, Mo, and W in air or Alzone, and with Pt in F. The combustion of Pt wire in a gaseous mixture of F (6/7 by vol) and Xe (1/7 by vol) produced a red-orange deposit on the walls. This color and the composition of the gas produced by the hydrolysis of the product are said to identify it as XePtF_6 (Bartlett, CA 57, 6850d). The yield is estimated at 50% of the Xe initially present.

63-82. Malm, John G., Ben D. Holt, and Ralph W. Bane

REACTIONS OF XENON FLUORIDES WITH AQUEOUS SOLUTIONS AND THE ISOLATION OF STABLE PERXENATES, pp. 167-73 in "Noble-Gas Compounds," H. H. Hyman, ed., Chicago, Univ. of Chicago Press, 1963.

The hydrolysis of XeF_2 produces a transient, bright yellow color; no combined xenon was recovered. Both XeF_4 and XeF_6 yield sparingly soluble perxenates in alkaline solution, which crystallize as hydrates. Solutions are usually yellow; most pure salts are white. In acid solution Xe(VIII) decomposes rapidly to Xe(VI) , liberating oxygen. In alkali solution, Xe(VI) disproportionates to Xe(VIII) and xenon.

63-83. Malm, J. G., I. Sheft, and C. L. Chernick

XENON HEXAFLUORIDE, J. Am. Chem. Soc. **85**, 110-11 (1963).

The preparation and properties of XeF_6 are reported. Yields of XeF_6 of greater than 90% were obtained by heating 5.25 mmole of Xe and 110 mmole of F for 16 hr at 300°C and about 60 atm in a nickel reaction vessel. The compound is a colorless solid, with a vapor pressure of about 7.5 mm at 0°C and of 30 mm at 25°C . It is stable at room temperature and reacts violently with hydrogen or water at room temperature. It

dissolves without reaction in anhydrous hydrogen fluoride. The infrared spectrum of the vapor was also studied.

63-84. Maričić, S., Z. Veksli, J. Slivnik, and B. Volavsek

MAGNETIC MEASUREMENTS ON XeF_4 , Croat. Chem. Acta. **35**, 77 (1963).

It is found that XeF_4 is diamagnetic from 77 to 293°K. Fluorine chemical-shift anisotropy is established by NMR.

63-85. Michels, H. H.

BINDING IN RARE-GAS COMPOUNDS, pp. 329-32 of "Noble-Gas Compounds," Chicago, Univ. of Chicago Press, 1963.

The relative importance of the various electron-correlation effects that occur in atomic and molecular systems of rare gases is examined. Special attention is given to radial-correlation effects between anti-parallel electron pairs.

63-86. Milligan, Dolphus E., and D. Sears

A SYNTHESIS OF XENON DIFLUORIDE NOT INVOLVING USE OF ELEMENTAL FLUORINE, J. Am. Chem. Soc. **85**, 823 (1963).

The successful synthesis of XeF_2 by high-voltage discharge in equimolar mixtures of Xe and CF_4 is reported. The experimental apparatus and the results of a typical run are described. Mass-spectrographic analysis confirmed the formula, and the infrared spectrum of the gaseous XeF_2 was measured.

63-87. Morton, J. R., and W. E. Falconer

ELECTRON SPIN RESONANCE SPECTRUM OF XeF IN γ -IRRADIATION XENON TETRAFLUORIDE, J. Chem. Phys. **39**, 427-31 (1963).

The radical XeF was detected by means of electron-spin resonance in a single crystal of XeF_4 γ irradiated at 77°K. The following hyperfine interaction constants were obtained for magnetic field directions parallel and perpendicular to the Xe-F bond: $^{19}\text{F}_\parallel = 2649$ Mc, $^{19}\text{F}_\perp = 540$ Mc, $^{129}\text{Xe}_\parallel = 2368$ Mc, and $^{129}\text{Xe}_\perp = 1224$ Mc. The unpaired electron occupies a σ orbital, and it was shown from parameters derived from the respective atomic wavefunctions that the orbital is predominantly F 2p and Xe 5p in character. The experimentally determined g values for XeF were $g_\parallel = 1.9740$ and $g_\perp = 2.1251$. Departures from the free-spin value are interpreted in terms of interaction between the orbital ground state and excited states of the molecule.

63-88. Neiding, A. B.

FLUORIDES OF XENON AND RADON, Uspekhi Khim. **32**, 501-7 (1963). (In Russian.)

The preparation of fluorides of xenon and radon is reviewed. A comparison of the noble gases with halides from the viewpoint of their electronegativity is presented.

63-89. Nesbet, R. K.

THEORY OF INERT-GAS FLUORIDES, J. Chem. Phys. **38**, 1783-4 (1963).

It is suggested that the principal binding mechanism in XeF_2 and XeF_4 is identical with the superexchange mechanism in antiferromagnetic oxides such as MnO . The theory is expressed in terms of localized ortho-normal transforms of Hartree-Fock molecular orbitals. The case of XeF_2 is considered in some detail. A table of parameters and binding energies is given for linear inert-gas difluorides. It is concluded that the formalism explains the stability of XeF_2 , and that, since stability increases with nuclear charge, RnF_2 should be more stable than XeF_2 , but none of the lighter inert-gas fluorides are stable.

63-90. Noyes, Richard M.

SOME PREDICTED CHEMISTRY OF GROUP VIII ELEMENTS: THE AEROGENS, J. Am. Chem. Soc. **85**, 2202-4 (1963).

The generic term aerogen is proposed for the elements of group VIII of the periodic table. The much greater ease with which the heavier aerogens form polyfluorides than polychlorides is more easily explained by the 3-center--4-electron description than by hybridization with d orbitals. A search for the hypothetical hydrides PH_3 and ClH_3 might provide evidence bearing on which bonding description of the aerogen polyhalides is more satisfactory. Aerogen oxides could be prepared by photolysis with ozone in condensed media. The aerogens may also react with ^1D sulfur atoms, and form gaseous complexes with the polyatomic Lewis acids BF_3 and SO_3 . The diatomic radical species NeF should be present in equilibrium concentration of the order of a percent in gas mixtures at a few atmospheres. With the possible exception of HeH , other diatomic radical species should be formed less easily. The aerogens might accept protons from strong gaseous Brønsted acids and form crystalline solids. Necessary proton-affinity data are not available, but it seems doubtful that such solids will form with the hydrogen halides. They may form with stronger gaseous proton acids.

63-91.

CHEMICAL PHYSICS, ORNL-3488, pp. 102-22, 1963.

A progress report covering work on many problems ... A neutron-diffraction study of single crystals of XeF_2 and XeF_4 gave accurate parameters for their molecular spacings. Anisotropic thermal analysis indicated similar libratory motion of the molecular species in these molecular crystals.

...The crystalline phase reported elsewhere as a "high-density form of XeF_4 " is shown, by crystal-structure analysis, to be a distinct compound with the composition $\text{XeF}_2 \cdot \text{XeF}_4$...

63-92. Perlow, G. J., C. E. Johnson, and M. R. Perlow

THE MÖSSBAUER EFFECT IN CHEMICAL COMPOUNDS OF ^{129}Xe , pp. 279-83 of "Noble-Gas Compounds," Chicago, Univ. of Chicago Press, 1963.

Measurements of the Mössbauer effect were made with the 40.0-keV $3/2^+ \rightarrow 1/2^+$ transition in ^{129}Xe , which follows the β decay of ^{129}I (1.6×10^7 yr). Measurements were made with hydroquinone clathrate containing

28% Xe by weight, sodium perxenat (nominally $\text{Na}_4\text{XeO}_6 \cdot 2\text{H}_2\text{O}$), XeF_4 , and XeF_2 . The clathrate and perxenat show a single line unshifted from zero velocity within experimental error. Both XeF_4 and XeF_2 show large and equal quadrupole splittings. No isomer shift was observed for either of them. All data were fitted and errors determined by the method of least squares. In both XeF_2 and XeF_4 , it was difficult to find a large enough source of the field gradient.

63-93. Pimentel, George C., and Richard D. Spratley
THE BONDING IN THE INERT GAS-HALOGEN COMPOUNDS--THE LIKELY EXISTENCE OF HELIUM DIFLUORIDE, *J. Am. Chem. Soc.* **85**, 826-7 (1963).

Pimentel's molecular-orbital description of trihalides is discussed with respect to its application to inert gas-halogen complexes. The vibrational frequencies and force constants of HeF_2 are predicted from these of HF_2^- .

63-94. Pitzer, Kenneth S.

BONDING IN XENON FLUORIDES AND HALOGEN FLUORIDES, *Science* **139**, 414-15 (1963).

The bonding in noble gas fluorides is comparable to that in halogen fluorides. Diatomic species such as ClF are considered as noble gas atoms, having their normal valence shells full. The addition of F_2 to ClF to form ClF_3 is analogous to the addition of F_2 to Xe to form XeF_2 . The stability of the halogen-fluorine bonds in the halogen polyfluorides is shown to depend on the ionization potential of the central atom. An extension of this theory predicts stable XeF_2 and XeF_4 molecules. Krypton fluorides are predicted to be thermodynamically unstable. Xenon oxides, analogous to ClO_2 or ClO_4^- , may be prepared by indirect methods, but are predicted to be unstable or even explosive.

63-95. Pomeroy, J. H.

POTENTIAL APPLICATIONS OF THE NOBLE-GAS COMPOUNDS, pp. 123-5 of "Noble-Gas Compounds," Chicago, Univ. of Chicago Press, 1963.

Speculation on the applications of the noble-gas compounds is presented.

63-96. Pysh, Eugene S., Joshua Jortner, and Stuart A. Rice.

FORBIDDEN ELECTRONIC TRANSITIONS IN XeF_2 AND XeF_4 , 64p., CONF-117-37, from American Chemical Society 145th National Meeting, New York, Sept 1963. (See 64-66.)

Transition strengths were measured for the weak 2330-Å band in XeF_2 ($f = 0.002$), and for the two weak bands in XeF_4 at 2280 Å ($f = 0.009$) and 2580 Å ($f = 0.003$). To investigate the origins of these weak transitions, the possibilities of vibronic and singlet-triplet transitions in XeF_2 and XeF_4 were examined. Using the Herzberg-Teller theory of vibronic transitions and a molecular-orbital treatment of excited electronic states, estimated strengths of the relevant vibronic transitions were calculated to be $f = 0.001$ for both XeF_2 and XeF_4 . The vibronic band in XeF_2 borrows intensity from the symmetry-allowed $^1A_{1g} \rightarrow ^1A_{2u}$ transition at 1580 Å ($f = 0.45$), whereas in XeF_4 the major

contribution to the vibronic bands from the symmetry-allowed $^1A_{1g} \rightarrow ^1E_u$ transition at 1325 Å ($f = 0.8$). A temperature dependence of the intensity of the 2330-Å band in XeF_2 was observed and found to be less than that predicted by the Herzberg-Teller theory. The estimated strength of the singlet-triplet transition in XeF_2 corresponding to the singlet-singlet transition at 1580 Å is shown to be small ($f \leq 10^{-4}$) in spite of a heavy-atom effect; the small transition strength persists because of the lack of nearby excited states of the required symmetry. In XeF_4 the triplet excited state 1E_u corresponding to the single-singlet transition $^1A_{1g} \rightarrow ^1E_u$ at 1840 Å ($f = 0.22$) is permitted by group-theoretical selection rules to mix with its own singlet state. Using an intermediate coupling scheme the estimated intensity of this singlet-singlet transition is calculated to be $f = 0.007$. The theoretical estimates of the symmetry and spin-forbidden transition strengths are used for the assignment of the weak electronic transitions in the xenon fluorides.

63-97. Reuben, J., D. Samuel, H. Selig, and J. Shamir
 ^{17}O -NUCLEAR MAGNETIC STUDY OF XENIC ACID, *Proc. Chem. Soc.* **270** (1963).

Hydrolysis of XeF_6 using ^{17}O -enriched water gave a colorless solution. Measurement of the ^{17}O NMR spectrum showed a chemical shift of -278 ± 2 ppm from water. Exchange of ^{17}O between the xenon-containing solution, xenic acid, $\text{Xe}(\text{OH})_6$, and water is extremely rapid.

The ^{17}O chemical shift for xenic acid is in the same range as for perchloric acid (-288), and the bromate, chlorate, and perchlorate ions (-297, -287 and -288).

63-98. Ruby, Stanley L.

MÖSSBAUER EFFECT IN KRYPTON, pp. 284-6 of "Noble-Gas Compounds," Chicago, Univ. of Chicago Press, 1963.

Properties of Kr which made it suitable for studies on Mössbauer effect are discussed.

63-99. Rundle, R. E.

ON THE PROBABLE STRUCTURE OF XeF_4 AND XeF_2 , *J. Am. Chem. Soc.* **85**, 112-13 (1963).

It is believed that the molecular structures of XeF_4 and XeF_2 may be predicted; reasons for this are given. Details of the proposed structure are illustrated and discussed. From the proposal it is expected that oxyluorides of Xe will contain pairs of linear F-Xe-F 3c-4e bonds.

63-100. Rutenberg, A. C.

XENON FLUORIDES: FLUORINE-19 NUCLEAR MAGNETIC RESONANCE SPECTRA, *Science* **140**, 993-4 (1963).

Chemical shifts were measured for liquid XeF_2 , XeF_4 , XeOF_4 , and XeF_6 , and ^{19}F - ^{129}Xe spin-spin coupling constants for XeF_4 and XeOF_4 . The data are in accord with reported structures and are similar to values in the literature for chemical shifts of fluorides of neighboring elements.

63-101. Sanderson, R. T.

THE COVALENT RADII OF XENON, *Inorg. Chem.* **2**, 660-1 (1963).

The bond length in XeF_4 is calculated from electro-negativity considerations for comparison with the observed value. From the XeF_4 electronegativity value of 4.05, the radius sum of Xe and F is computed to be 2.12 Å, or 1.95 Å for single Xe-F bonds. This latter value is in good agreement with the observed value of 1.92 ± 0.03 Å. The bond lengths in XeF_2 and KrF_4 are predicted to be ~2.11 and ~1.84 Å, respectively.

63-102. Sheft, Irving, and H. H. Hymen

FLUORINE EXCHANGE BETWEEN XENON HEXAFLUORIDE AND GASEOUS FLUORINE, pp. 68-70 of "Noble-Gas Compounds," Chicago, Univ. of Chicago Press, 1963.

The rate of exchange of fluorine between XeF_6 and gaseous fluorine was found to be a linear function of fluorine concentration and to extrapolate back through zero. In a single exchange between 0.014 mole/liter XeF_6 and 1.10 moles/liter F_2 at 100°C , a rate of exchange of 0.078×10^{-3} mole liter $^{-1}$ min $^{-1}$ was obtained. An activation energy of 20 kcal/mole, was calculated from the results. Although the results of the XeF_6 - F_2 exchange experiments do not completely rule out an association complex with fluorine atoms, the data are best explained by an exchange mechanism involving a complex with fluorine molecules.

63-103. Siegel, Stanley, and Elizabeth Gebert

CRYSTALLOGRAPHIC STUDIES OF XeF_2 AND XeF_4 , *J. Am. Chem. Soc.* **85**, 240 (1963).

The structure of XeF_2 prepared by a photochemical process is described and crystallographic data on XeF_4 presented. XeF_2 is tetragonal with $a = 4.315 \pm 0.003$ Å and $c = 6.990 \pm 0.004$ Å. Crystals condensed from XeF_4 vapor at room temperature were found to exhibit more than one symmetry. A monoclinic form frequently observed has the dimensions $a = 5.03$ Å, $b = 5.92$ Å, $c = 5.79$ Å, and $\beta = 99^\circ 27'$.

63-104. Siegel, S., and E. Gebert

CRYSTALLOGRAPHIC STUDIES OF XENON DIFLUORIDE, XENON TETRAFLUORIDE, AND SOME SODIUM XENATE HYDRATES, pp. 193-4 of "Noble-Gas Compounds," Chicago, Univ. of Chicago Press, 1963.

XeF_2 is tetragonal with $a = 4.315 \pm 0.003$ and $c = 6.900 \pm 0.004$ Å. The space group is $14_2/mmm$ with Xe atoms in 0, 0, 0; $1/2, 1/2, 1/2$, and F atoms in $00z$, $00\bar{z}$ + b.c. The two molecules in the cell lead to a density of 4.32 g/cc. A value $z = 0.306 \pm 0.02$ determined by X rays leads to linear F-Xe-F molecules with Xe-F = 2.14 ± 0.14 Å. XeF_4 crystals are monoclinic with $a = 5.03$, $b = 5.92$, and $c = 5.79$ Å, and $\beta = 99^\circ 27'$. The space group is $P2_1/n$ with Xe atoms in 0, 0, 0; $1/2, 1/2, 1/2$, and F atoms in general positions. The computed density based on the two molecules in the cell is 4.04 g/cc. A planar character for the molecule is indicated by the symmetry. The hydrolysis product, $\text{Na}_4\text{XeO}_6 \cdot 5\text{H}_2\text{O}$, (now established as $\text{Na}_4\text{XeO}_6 \cdot 8\text{H}_2\text{O}$) was found to be orthorhombic with $a = 10.36$, $b = 10.45$, and $c = 11.87$ Å. A product of

composition, $\text{Na}_4\text{XeO}_6 \cdot 2\text{H}_2\text{O}$, is also orthorhombic with $a = 6.25$, $b = 5.77$, and $c = 10.28$ Å.

63-105. Slivnik, J., B. Volavšek, J. Marsel, V. Vrščaj, A. Šmalc, B. Frelec, and Z. Zemljčič

ON THE SYNTHESIS OF XeF_8 , *Croat. Chem. Acta.* **35**, 81-2 (1963). (In German.)

Conditions of xenon fluoride formation are studied, and the pressure of the reaction mixture $\text{Xe}:\text{F} = 1:20$ was measured in the temperature range between 20 to 620°C . In addition to previously reported XeF_6 , a new reaction product is observed. The fluorine analysis of this product corresponds to the formula XeF_8 (F:Xe ratio is 8.1 ± 0.1). In a sealed tube, at room temperature, this substance is an unstable, pale yellow gas. Upon cooling with liquid nitrogen the gas converts into a yellow solid phase.

63-106. Slivnik, J., B. Volavšek, J. Marsel, V. Vrščaj, A. Šmalc, B. Frlec, and A. Zemljčič

ON THE SYNTHESIS OF HIGHER XENON FLUORIDES, pp. 64-7 of "Noble-Gas Compounds," Chicago, Univ. of Chicago Press, 1963.

A method and conditions for the preparation of higher fluorides, XeF_6 and XeF_8 , are reported.

63-107. Sloth, E. N., and M. H. Studier

GASEOUS KRYPTON FLUORIDE, *Science* **141**, 528 (1963).

Mass-spectrometric analysis of a krypton fluoride prepared by the method used for preparing KrF_4 showed only Kr^+ and KrF^+ , indicating the parent ion was most probably KrF_2 .

63-108. Smith, D. F.

XENON TRIOXIDE, *J. Am. Chem. Soc.* **85**, 816-17 (1963).

The preparation of the explosive compound XeO_3 by slow hydrolysis of XeF_6 is described. Neutron activation analysis and infrared spectra show no fluorine in XeO_3 . The decomposition reaction is found to be $\text{XeO}_3 \rightarrow \text{Xe} + 3/2 \text{O}_2$, with small amounts of CO_2 due to reaction of O_2 with carbon-containing material. The deliquescence behavior of XeO_3 at high humidities is described briefly.

63-109. Smith, D. F.

XENON DIFLUORIDE, *J. Chem. Phys.* **38**, 270-1 (1963).

The preparation, purification, and identification of XeF_2 is reported. It is a colorless solid with a vapor pressure comparable to that of XeF_4 , about 3 mm at room temperature. It can be sublimed easily at room temperature to give weakly birefringent rhombohedrons, along with a few three- and six-sided crystal figures. The spectrum of XeF_2 at 100°C with nearly saturated vapor pressure showed a band at 1070 cm^{-1} , with no discernible Q branch, and a P-R peak separation of 15 cm^{-1} .

63-110. Smith, D. F.

THE USE OF INFRARED SPECTROSCOPY IN THE PREPARATION AND STUDY OF XENON COMPOUNDS, pp. 39-46 of "Noble-Gas Compounds," Chicago, Univ. of Chicago Press, 1963.

A circulating loop containing an infrared cell located in a spectrophotometer beam was designed for studying the corrosive fluorine-containing gases and their volatile reaction products. The loop was used to study Xe-F_2 and $\text{XeF}_2\text{-F}_2$ reactions and to prepare small quantities of fairly pure XeF_2 . It was also used to test the purity and to improve the purity of XeF_2 , XeF_4 , and XeF_6 preparations. Small quantities of XeOF_4 were prepared by the hydrolysis of XeF_6 , and the vapor pressure as a function of temperature was determined for XeOF_4 and the xenon fluorides. A schematic diagram of the loop is presented.

63-111. Smith, D. F.

INFORMATION ON BONDING IN XENON COMPOUNDS FROM INFRARED SPECTRA, pp. 295-303 in "Noble-Gas Compounds," H. H. Hyman, ed., Chicago, Univ. of Chicago Press, 1963.

From observation of the infrared absorption spectra, it may be concluded that XeF_2 is a linear molecule, Xe_4 is a square planar molecule, and XeF_6 is probably not octahedral. XeOF_4 is a square pyramid with the O attached in a double bond above the Xe in an XeF_4 arranged as in that compound. The force constant and particularly the interaction constants do not correspond to those found for ICl_2^- , the classical example of the three-center bond of the type expected for XeF_2 . The results are interpreted in terms of a larger-than-predicted contribution of the Xe 5d orbitals to the hybrid molecular orbitals and a correspondingly smaller ionic contribution than in the ICl_2^- case.

63-112. Smith, D. F.

INFRARED SPECTROSCOPY OF XENON COMPOUNDS, TID-19201, 1963, 16p.

Infrared spectroscopy has been an important factor in the development of the new field of inert gas chemistry. A discussion is presented of some aspects of infrared spectroscopy in this field. Techniques employed in studying the Xe compounds are described, and their use in the study of XeF_2 , XeF_4 , XeF_6 , and XeOF_4 is illustrated. The particular features of the spectrum and the molecular configuration are discussed.

63-113. Smith, D. F.

XENON OXYFLUORIDE, Science 140, 899-900 (1963).

The incomplete hydrolysis of XeF_6 was used to prepare a xenon oxyfluoride, XeOF_4 . The latter is a clear, colorless liquid, freezing at -41°C . The infrared and Raman spectra show that the XeOF_4 molecule has a fourfold symmetry axis. The large Xe-O stretching force constant indicates the Xe-O bond has appreciable double bond character.

63-114. Smith, R. B.

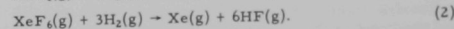
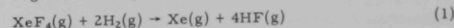
SAFETY PRECAUTIONS IN HANDLING NOBLE-GAS COMPOUNDS, pp. 126-9 of "Noble-Gas Compounds," Chicago, Univ. of Chicago Press, 1963.

A set of interim safeguards are suggested for handling XeO_3 and xenon fluorides and oxyfluorides. Also, until such time as adequate hazard knowledge and experience are developed locally to warrant lesser precautions, the safeguards are suggested for all other noble gas compounds.

63-115. Stein, L., and P. L. Plurien

THERMOCHEMICAL STUDIES OF XENON TETRAFLUORIDE AND XENON HEXAFLUORIDE, pp. 144-8 in "Noble-Gas Compounds," Chicago, Univ. of Chicago Press, 1963.

The reduction of xenon tetrafluoride and xenon hexafluoride with hydrogen is being studied with an isothermal calorimeter at 120 to 130°C . Each compound reacts rapidly with hydrogen in this temperature region, forming xenon and hydrogen fluoride:



Preliminary values of the heats of reaction obtained thus far are $\Delta H = -202$ kcal/mole XeF_4 for reaction 1 and $\Delta H = -306$ kcal/mole XeF_6 for reaction 2. The approximate heats of formation are calculated to be:

$$\Delta H_f \text{XeF}_4(\text{g}) = -55 \text{ kcal/mole}$$

and

$$\Delta H_f \text{XeF}_6(\text{g}) = -79 \text{ kcal/mole}.$$

From the present measurements the average xenon-fluorine bond energy is found to be 32.0 kcal in the tetrafluoride and 31.5 kcal in the hexafluoride.

63-116. Streng, A. G., A. D. Kirshenbaum, L. V. Streng, and A. V. Grosse

PREPARATION OF RARE-GAS FLUORIDES AND OXYFLUORIDES BY THE ELECTRIC-DISCHARGE METHOD AND THEIR PROPERTIES, pp. 73-80 of "Noble-Gas Compounds," Chicago, Univ. of Chicago Press, 1963.

A number of noble-gas compounds were prepared with the aid of an electric discharge: with xenon and fluorine alone, XeF_4 and XeF_6 ; with krypton and fluorine, KrF_4 ; with xenon and oxygen difluoride, XeOF_2 . A product containing one or more compounds having the approximate formula XeOF_3 was prepared by heating Xe and OF_2 .

63-117. Streng, A. G., and A. V. Grosse

ACID OF KRYPTON AND ITS BARIUM SALT, Science 143, 242-3 (1963).

An acid of krypton is formed when KrF_4 is slowly hydrolyzed by ice at -30 to -60°C . The yield is 2 to 3 mole %. A barium salt of this acid, thermally stable at room temperature, is formed by the hydrolysis of krypton tetrafluoride with a 0.35 N solution of $\text{Ba}(\text{OH})_2$ at 10 to 5°C in a yield of approximately 7 wt %.

63-118. Studier, M. H., and E. N. Sloth

GASEOUS FLUORIDES OF XENON, *J. Phys. Chem.* **67**, 925-6 (1963).

Mass-spectrometric analyses were carried out on the ions produced by electron bombardment of the vapors from solid XeF_4 . The following ions were identified: Xe^+ , XeF^+ , XeF_2^+ , XeF_3^+ , XeF_4^+ , Xe_2^+ , XeF_2^{2+} , XeF_3^{2+} , XeF_4^{2+} , XeO^+ , XeOF^+ , XeOF_2^+ , XeOF_3^+ , and XeOF_4^+ . The ions XeF_2^+ , XeF_4^+ , XeOF_2^+ , and XeOF_4^+ probably arise from independent neutral species, whereas the others are fragmentation products. It is concluded that XeF_2 exists as an independent species of greater volatility than XeF_4 . The possible existence of XeOF_3 and XeOF_4 is discussed.

63-119. Studier, Martin H., and Eric N. Sloth

MASS-SPECTROMETRIC STUDIES OF NOBLE-GAS COMPOUNDS, pp. 47-9 of "Noble-Gas Compounds," Chicago, Univ. of Chicago Press, 1963.

Mass-spectrometric studies were made of Xe , XeF_4 , XeF_2 , and XeF_6 . The formula of the oxyfluoride XeOF_4 was deduced from its mass and the complexity of the fragmentation pattern caused by loss of either oxygen or fluorine atoms. No spectrum attributable to XeF_3 was observed, although copious evolution of Xe and O suggested the presence of an oxide.

63-120. Svec, Harry J., and Gerald D. Flesch

THERMOCHEMICAL PROPERTIES OF XENON DIFLUORIDE AND XENON TETRAFLUORIDE FROM MASS SPECTRA, *Science* **142**, 954-5 (1963).

The standard heats of formation for gaseous XeF_4 and XeF_2 , and the average strength of the bonds in these molecules, were determined from appearance-potential data obtained with a mass spectrometer. The experimental values are compatible with theoretical estimates of these quantities.

63-121. Tanaka, Toshio, and Yoshikane Kawasaki

COMPOUNDS WITH ABNORMAL VALENCIES, *Kagaku* (Kyoto) **18**, 746-50 (1963). (In Japanese.)

This paper consists of a report of a meeting concerned with abnormal valence compounds, such as boron hydrides, carbonyls, ferrocene-type compounds, and noble gas compounds. The structures of the noble gas compounds are reviewed and discussed in terms of molecular-orbital theory and electron-pair, valence-bond theory.

63-122. Templeton, David H., Allan Zalkin, J. D. Forrester, and Stanley M. Williamson

CRYSTAL AND MOLECULAR STRUCTURE OF XENON TETRAFLUORIDE, *J. Am. Chem. Soc.* **85**, 242 (1963).

The crystal structure of XeF_4 was determined by X-ray diffraction at room temperature. The structure consists of a molecular packing of square-planar molecules of XeF_4 . The monoclinic unit cell has dimensions $a = 5.050$, $b = 5.922$, $c = 5.771$ Å (each ± 0.003 Å), and $\beta = 99.6^\circ \pm 0.1^\circ$. With 2 molecules per cell the density is 4.04 g/ml. Intensities were measured for the 329 independent reflections of the primitive cell with θ less than 25° . Of these, 36 were

absent because of the space-group symmetry. Calculations gave Xe-F bond distances of 1.92 and 1.90 Å.

63-123. Templeton, D. H., A. Zalkin, J. D. Forrester, and S. M. Williamson

CRYSTAL AND MOLECULAR STRUCTURE OF XENON TRIOXIDE, *J. Am. Chem. Soc.* **85**, 817 (1963).

The chemical formula of XeO_3 was confirmed by adding KI to an acidified aqueous solution of XeO_3 and measuring the liberated iodine and xenon. Crystal data were obtained from oscillation and Weissenberg X-ray diffraction photographs. The orthorhombic unit cell has the dimensions $a = 6.163 \pm 0.008$, $b = 8.115 \pm 0.010$, $c = 5.234 \pm 0.008$ Å. The Xe-O bond distances are 1.74, 1.76, and 1.77 ± 0.03 Å. The O-Xe-O bond angles are 108, 100, and $101 \pm 2^\circ$.

63-124. Templeton, David H., Allan Zalkin, J. D. Forrester, and Stanley M. Williamson

DETERMINATION OF THE CRYSTAL STRUCTURE OF XENON TRIOXIDE, pp. 229-237 in "Noble-Gas Compounds," Chicago, University of Chicago Press, 1963.

XeO_3 was characterized by determination of its crystal and molecular structure by X-ray diffraction by single crystals. Four molecules of XeO_3 occupy an orthorhombic cell in space group $P2_12_12_1$ with dimensions $a = 6.163 \pm 0.008$ Å, $b = 8.115 \pm 0.010$ Å, $c = 5.234 \pm 0.008$ Å. The crystal structure is closely related to that of the isoelectronic HIO_3 . The XeO_3 molecule has trigonal pyramidal shape with average Xe-O bond length 1.76 Å (corrected for thermal motion) and average O-Xe-O bond angle 103° .

63-125. Templeton, David H., Allan Zalkin, J. D. Forrester, and Stanley M. Williamson

A DETERMINATION OF THE CRYSTAL STRUCTURE OF XENON TETRAFLUORIDE, pp. 203-210 in "Noble-Gas Compounds," Chicago, University of Chicago Press, 1963.

The crystal and molecular structure of XeF_4 were determined by single-crystal X-ray diffraction techniques. The intensities of $\text{MoK}\alpha$ X rays diffracted by the crystal were measured with a scintillation counter. The monoclinic unit-cell dimensions are $a = 5.050$ Å, $b = 5.922$ Å, $c = 5.771$ Å (each ± 0.003 Å), and $\beta = 99.6^\circ \pm 0.1^\circ$. The space group is $P2_1/n$ with two molecules per unit cell. The xenon atoms occupy the corners and body centers, so that the molecular packing is pseudo body-centered cubic. The molecule has a square planar configuration. The Xe-F bond distance is 1.93 ± 0.02 Å, after a correction of $+0.02$ Å for thermal-vibration effects; the F-Xe-F bond angle is a right angle ($90.4 \pm 0.9^\circ$) within the accuracy of the determination.

63-126. Tommila, Eero

CHEMICAL COMPOUNDS OF INERT GASES, Suomen Kemistilehti **A36**, 209-19 (1963). (In Finnish.)

A review of noble gas chemistry; 96 references.

63-127. Turner, J. J., and G. C. Pimentel

PREPARATION OF INERT-GAS COMPOUNDS BY MATRIX ISOLATION: KRYPTON DIFLUORIDE, pp. 101-5 of "Noble-Gas Compounds," Chicago, Univ. of Chicago Press, 1963.

A method for the preparation of KrF_2 by matrix isolation is described. The force constants of KrF_2 were found to be close to those of XeF_2 . It was concluded that the matrix-isolation technique is a useful preparative method for inert-gas compounds, and it may have unique value for those that are least stable.

63-128. Turner, J. J., and George C. Pimentel

KRYPTON FLUORIDE: PREPARATION BY THE MATRIX ISOLATION TECHNIQUE, Science **140**, 974-5 (1963).

A method is described for the preparation of KrF_2 by the photolysis of fluorine suspended in a solid mixture of argon and krypton at 20°K. This experimental method is called the matrix-isolation technique.

63-129. Ward, Roland

WOULD MENDELEEV HAVE PREDICTED THE EXISTENCE OF XeF_4 ?, J. Chem. Ed. **40**, 277-279 (1963).

The bimay fluorides in which the central atoms use sp^3 , sp^3d , and sp^3d^2 hybrid orbitals for bonding are tabulated. Extrapolations to stable XeF_2 , XeF_4 , KrF_2 , and KrF_4 seem reasonable. By comparison with halogen fluorides, stable compounds are predicted to be ArF_2 , KrF_2 , KrF_4 , XeF_4 , XeF_6 , RnF_4 , and RnF_6 . XeF_2 and RnF_2 are predicted to be "unstable." A discussion of possible fluoro anions of noble gases suggests XeF_3^- as a candidate.

63-130. Waters, James H., and Harry B. Gray

BOND ENERGIES AND IONIC CHARACTER OF INERT GAS HALIDES, J. Am. Chem. Soc. **85**, 825-6 (1963).

An adaptation of simple molecular-orbital theory is used to calculate stabilities of some inert gas halides. Dissociation energies are tabulated for a number of possible fluorides and chlorides of neon, argon, krypton, and xenon. The model predicts stability for KrF_4 , with KrF_2 , XeCl_4 , and ArF_4 being marginal. The bond-energy decrease for the fluorides is relatively small from xenon to argon. However, the change from argon to neon is so great that neon halides are thought unlikely to exist. The results show that no special bonding assumptions are needed for the inert gas halides; they fit naturally into the sequence of non-metallic elements in their higher valence states.

63-131. Weaver, E. Eugene, Bernard Weinstock, and Charles P. Knop

XENON HEXAFLUORIDE, J. Am. Chem. Soc. **85**, 111-12 (1963).

The preparation and properties of XeF_6 are reported. Reactions were carried out in a stainless steel vessel at 1000 psi and 350 to 450°C. In all cases a mixture of volatile products was obtained. The more volatile fractions always concentrated XeF_6 . The purity of the samples was monitored by infrared spectroscopy. In the purest XeF_6 sample, the twin bands $\nu_2 + \nu_3$ and $\nu_1 + \nu_3$ were observed at 1154 and 1189 cm^{-1} . The formula for

XeF_6 was established by chemical analysis. The compound can be reduced with H_2 to form HF and Xe. Preliminary vapor pressure measurements gave: 0°C, 6 mm; and 20°C, 27 mm.

63-132. Weeks, James L., and Max S. Matheson

PHOTOCHEMISTRY OF THE FORMATION OF XENON DIFLUORIDE, pp. 89-97 of "Noble-Gas Compounds," Chicago, Univ. of Chicago Press, 1963.

Xenon and fluorine combine photochemically when irradiated with near ultraviolet light in the fluorine absorption band. If the product is continuously trapped out, essentially pure XeF_2 is produced. Fluorine and XeF_2 will further react photochemically to produce XeF_4 . Quantum yields for XeF_2 formation are of the order of 0.3 to 0.7, being somewhat lower at higher pressures, especially at higher pressures of fluorine. The mechanism of formation very probably involves fluorine atoms. A transient intermediate, perhaps XeF , was detected in flash-photolysis experiments. Attempts at the photochemical preparation of other rare gas compounds have not yet been successful.

63-133. Weinstock, Bernard, E. Eugene Weaver, and Charles P. Knop

THE XENON-FLUORINE SYSTEM, pp. 50-60 of "Noble-Gas Compounds," Chicago, Univ. of Chicago Press, 1963.

In a method of preparation for XeF_6 , Xe and F were reacted at a high temperature and the products formed were rapidly cooled to a lower temperature. In the initial preparations the ratio of fluorine to Xe was varied from 6 to 40, and their combined starting pressure was 1000 psi. Reaction temperatures in the range 350-450°C were provided by an electrically heated nickel-gauze filament and the reactor wall kept either at -115 or at 80°C to provide the quenching. XeF_6 was produced in all of the experiments, as well as XeF_2 , XeF_4 , and another xenon fluoride that was not immediately characterized. The presence of the compounds was qualitatively monitored by infrared spectroscopy. XeF_6 was identified with a strong absorption at 610 cm^{-1} , XeF_2 with bands at 551 cm^{-1} and 567 cm^{-1} , and XeF_4 with bands at 582 and 592 cm^{-1} . The spectrum of the unidentified compound showed a broad absorption system with a characteristic maximum at 520 cm^{-1} . Evidence strongly suggests that the compound at 520 cm^{-1} is XeF_5 . However, it is pointed out that while the evidence is strongly suggestive of this formula, it is still incomplete.

63-134. Williamson, Stanley M., and Charles W. Koch

THE REACTION OF XENON TETRAFLUORIDE WITH AQUEOUS SOLUTION: CHEMISTRY OF XENON TRIOXIDE, pp. 158-66 of "Noble-Gas Compounds," Chicago, Univ. of Chicago Press, 1963.

The hydrolysis of XeF_4 in aqueous solutions was studied. In addition to the direct oxidation of water by XeF_4 to give oxygen, xenon, and hydrofluoric acid, the reaction also gave a very soluble xenon(VI) species. The decomposition, chemical properties, and reactions of XeO_3 are discussed.

63-135. Williamson, Stanley M., and Charles W. Koch
XENON TETRAFLUORIDE: REACTION WITH
AQUEOUS SOLUTIONS, *Science* **139**, 1046-7 (1963).

XeF_4 reacts with water to yield xenon, oxygen, HF , and a very soluble species containing xenon. Evaporation of the solution yields a white, crystalline substance which was identified as xenon(VI) oxide, XeO_3 .

63-136. Wilson, E. G., Joshua Jortner, and Stuart A. Rice

A FAR-ULTRAVIOLET SPECTROSCOPIC STUDY OF XENON DIFLUORIDE, *J. Am. Chem. Soc.* **85**, 813-14 (1963).

The absorption spectrum of XeF_2 in the gas phase was studied in the uv region to 1100 Å. A weak band was found at 2300 Å, while strong absorption at 1580 Å was observed, followed by sharp bands at 1425, 1335, 1215, and 1145 Å. The results are interpreted in terms of the bonding in XeF_2 . The strong 1580-Å absorption is assigned to the first singlet-singlet allowed transition $\sigma_g \rightarrow \sigma_u^+$. The weak 2300-Å band probably arises from a singlet-singlet transition $\pi_u \rightarrow \sigma_u^+$. The sharp bands are assigned to Rydberg states, and the first ionization potential is calculated to be 11.5 ± 0.2 eV.

63-137. Yamada, Soichiro

THE MOLECULAR STRUCTURES OF COMPOUNDS OF RARE-GAS ELEMENTS, *Rev. Phys. Chem. Japan* **33**, 39-40 (1963).

The valence bond-lone pair theory is used to provide simple, qualitative predictions of the shapes of noble-gas compounds. The configurations of XeO_3 , XeF_2 , XeF_4 and KrF_4 , XeF_3^+ , and XeF_6 are, respectively, trigonal pyramid, linear, square plane, square pyramid, and distorted octahedron.

63-138. Yost, Don M.

A NEW EPOCH IN CHEMISTRY, pp. 21-22 in "Noble-Gas Compounds," H. H. Hyman, ed., Chicago, University of Chicago Press, 1963.

Reminiscence, philosophy, and a little prognostication.

63-139. Zalkin, Allan, J. D. Forrester, David H. Templeton, Stanley M. Williamson, and Charles W. Koch

SODIUM PERXENATE HEXAHYDRATE, *Science* **142**, 501-2 (1963).

Sodium perxenate hexahydrate ($\text{Na}_4\text{XeO}_6 \cdot 6\text{H}_2\text{O}$) was identified from study of its crystal structure by X-ray diffraction. The perxenate ion (XeO_6^{4-}) has the shape of a regular octahedron with the Xe-O bond distance 1.84 Å.

1964

64-1. Adrian, Frank J.

THEORY OF THE NUCLEAR MAGNETIC RESONANCE CHEMICAL SHIFT OF Xe IN XENON GAS, *Phys. Rev.*, **136**: A980-7 (Nov. 16, 1964).

A theoretical study is made of the density-proportional paramagnetic shift of the resonant magnetic field

observed in nuclear magnetic resonance studies of ^{129}Xe in pure xenon gas by Streever and Carr. The theory is based on a computation of the chemical shift in diatomic molecules formed by colliding Xe atoms, including the effects of van der Waals and exchange interactions on the wave function of the colliding atoms. The results of this calculation show that only the exchange interactions between the colliding atoms make a significant contribution to the chemical shift. When averaged over the various types of collisions, the following value is obtained for the shift in the resonant field: $\Delta H = -2.85(10)^{-7} H\rho$, where H is the field strength and ρ is the density in amagats. This is in order-of-magnitude agreement with the observed result: $\Delta H = -4.3(10)^{-7} \rho H$.

64-2. Appelman, E. H., and J. G. Malm

HYDROLYSIS OF XENON HEXAFLUORIDE AND THE AQUEOUS SOLUTION CHEMISTRY OF XENON, *J. Am. Chem. Soc.* **86**, 2141-8 (1964).

Both XeF_4 and XeF_6 hydrolyze in water to produce aqueous solutions of nonvolatile XeO_3 molecules. The solutions are stable, but they are strongly oxidizing, rapidly liberating chlorine from strong HCl . The Xe-Xe(VI) potential is estimated to be 1.8 V in acid and 0.9 V in base. The XeO_3 molecule is a weak acid, forming XeO_4^- above pH 10.5. In strongly basic solution Xe(VI) disproportionates to give xenon gas and octavalent xenon, whereas in such solutions ozone oxidizes Xe(VI) nearly quantitatively to Xe(VIII) . Sodium and Ba salts of Xe(VIII) perxenates were characterized, with typical compositions $\text{Na}_4\text{XeO}_6 \cdot 2.2\text{H}_2\text{O}$ and $\text{Ba}_2\text{XeO}_6 \cdot 1.5\text{H}_2\text{O}$. A salt of mixed oxidation state, $\text{K}_4\text{XeO}_6 \cdot 2\text{XeO}_3$, was also observed. Aqueous solutions of sodium perxenate evolve oxygen slowly to give Xe(VI) . The reaction becomes almost instantaneous below pH 7. Octavalent xenon is an extremely powerful oxidizing agent, rapidly oxidizing iodate to periodate and Mn^{2+} to permanganate. The Xe(VI)-Xe(VIII) potential is estimated at 3.0 V in acid and 0.9 V in base. In basic solution Xe(VIII) is present as the ion HXeO_6^{4-} . Below pH 10 the principal species becomes $\text{H}_2\text{XeO}_6^{2-}$. Both Xe(VI) and Xe(VIII) have characteristic, pH-dependent, ultraviolet absorption spectra that can be attributed to the several species present. (For correction see 67-5.)

64.3. Appelman, Evan H., and John G. Malm

CHARACTERIZATION OF DIVALENT XENON IN AQUEOUS SOLUTION, *J. Am. Chem. Soc.* **86**, 2297-8 (1964).

XeF_2 was hydrolyzed in 20 ml of water to yield a colorless solution with a pungent odor. It was analyzed 50 min after mixing and was found to contain 4.6 mequiv of oxidizing power, which at 0°C was lost with a half-life of about 7 hr. Extrapolation to the time of mixing gave an initial yield of 5.0 mequiv or 87% of the oxidizing power present in the XeF_2 . At room temperature the decomposition was much faster. After 30 hr at ca 24°C, less than 0.03% of the original oxidizing power remained. The decomposed solution was found to contain 5.62 mmoles of HF , compared to 5.76 mmoles calculated from the weight of XeF_2 taken. The gases evolved on decomposition of this solution were found to consist of Xe and O_2 in the ratio 2.08:1. It was concluded that XeF_2 dissolves in water to the extent of

about 0.15 M and is present in solution as undissociated molecules, which do not form complex anions with F^- .

64-4

OTHER NUCLEAR EXPERIMENTS, ANL-6879,
p. 69-87 (1964).

The hyperfine structures of several nuclei were investigated. The Mössbauer effect was observed in ^{119}Sn and ^{57}Fe metals, Mg-Sn alloy, Gd, Nb_3Sn , K₂Fe-V alloy, and Xe compounds. Also, the properties of ^{188}Re and ^{129}Xe levels were determined from observations of appropriate decay schemes. ^{116}Sn levels populated in the decay of ^{116}Sb and ^{116}In were studied, together with ^{66}Ga levels populated by the decay of ^{66}Ge . A fission of the ^{252}Cf into three fragments was apparently observed. Further measurements were made of muonic X rays. The K X rays of Al, Mg, V, Fe, Zn, and Ni were measured with high precision, as well as the L X rays of V, Fe, Zn, Cu, and Ni. The K and L X-ray spectra of Th, ^{239}Pu , ^{235}U were obtained; similar measurements were made with Bi, Ta, and Au.

64-5

ARGONNE'S CONTRIBUTION TO XENON CHEMISTRY,
Argonne Natl. Lab. Rev. 1 (No. 4), 17-19 (Oct 1964).

A review is presented of the discovery and development of xenon compounds. Safety procedures are suggested for working with xenon and its compounds, particularly xenon fluorides and oxides.

64-6. Baker, B. G., and P. G. Fox

CATALYSED REACTION OF XENON WITH FLUORINE,
Nature 204, 466-7 (1964).

It is found that Ni, and to a lesser extent Cu and Al, have a catalytic effect on the production of xenon fluorides from mixtures of Xe and F.

64-7. Barabas, E.

CHEMICAL COMPOUNDS OF THE INERT GASES,
Studii Cercetari Chim. 12(2), 153-68 (1964).
(In Rumanian.)

A review. 67 references.

64-8. Bartlett, N.

THE CHEMISTRY OF THE NOBLE GASES, Endeavour
23, 3-7 (1964).

The preparation chemistry and structure of rare gas compounds are reviewed. An assessment of the range of compounds that the various rare gases can be expected to form is given.

64-9. Bartlett, Neil

NOBLE-GAS COMPOUNDS, Intern. Sci. Technol.,
No. 33, 56-62, 64, 66 (1964).

The prediction and verification of rare-gas compounds are reviewed, together with the bases for the previous contention of no reaction in these gases. The structure and chemistry of rare-gas compounds are then discussed, with particular emphasis on bonding theories.

64-10. Bilham, J., and J. W. Linnett

ELECTRONIC STRUCTURE OF XENON DIFLUORIDE,
Nature 201, 1323 (1964).

The results of calculations relating to the electronic structure of XeF_2 are reported. The treatment is of the four electrons associated with a framework $F^+Xe^{2+}F^+$. The wave functions of the molecule were constructed from the $2p_z$ orbitals of the two fluorine atoms and the $5p_z$ orbital on the xenon atom. The three atoms are in a straight line along the z-axis. It was assumed that other atomic orbitals can be neglected.

64-11. Blinc, R., I. Zupančič, S. Maričič, and
Z. Vekslj

SIGN OF THE SHIELDING ANISOTROPY IN XENON
TETRAFLUORIDE, J. Chem. Phys. 40, 3739 (1964).

This short note indicates that the previously reported absolute value of the ^{19}F magnetic shielding anisotropy in XeF_4 could now be reported as $-(570 \pm 40)$ ppm.

64-12. Bohn, Robert Karl

ELECTRON DIFFRACTION STUDIES OF MOLECULAR
STRUCTURE: CIS- AND TRANS-DIFLUORODIAZINE
DIFLUOROAMINO RADICAL AND TETRAFLUORO-
HYDRAZINE, XENON TETRAFLUORIDE AND XENON
HEXAFLUORIDE, Thesis, Ithaca, N. Y., Cornell Univ.,
1964. 118p.

Electron-diffraction photographs of gaseous samples of the two isomers of difluorodiazine, the difluoroamino radical, tetrafluorohydrazine, XeF_4 , and xenon hexafluoride were taken with a rotating-sector apparatus. The diffraction intensities were reduced quantitatively, and the structures were deduced from both radical-distribution analyses and quantitative comparisons of theoretical with experimental intensities. The structure of the less reactive isomer of difluorodiazine is a trans configuration. The reactive isomer of difluorodiazine was confirmed to have a cis configuration. There is a small difference between the N-F bond lengths as determined by electron diffraction, 1.409 ± 0.013 Å, and from microwave spectra, 1.384 ± 0.010 Å. The structural parameters for trans- and cis- N_2F_2 are listed. The major structural difference between the two isomers is in the NNF angle. The structure of tetrafluorohydrazine was found to be like that of hydrazine. Structural parameters for NF_2 and N_2F_4 are listed. The major structural difference between the two compounds is the larger N-F bond length in tetrafluorohydrazine. It appears that the odd electron in the radical contributes π -bonding character to the N-F bond. The structure of XeF_4 is a square planar configuration. Preliminary data were obtained on the structure of XeF_6 . The results indicate that the structure has less than octahedral symmetry. The structural parameters for XeF_4 and XeF_6 are listed. A survey of theories of bonding in the rare gas compounds is presented. A method of analysis of electron-diffraction photographs for the determination of molecular structures is described in detail.

64-13. Boudreaux, Edward A.

ON THE MAGNETIC SUSCEPTIBILITY OF XENON TETRAFLUORIDE, *J. Chem. Phys.* **40**, 229-32 (1964).

The magnetic susceptibility of XeF_4 was treated theoretically in the LCAO-MO approximation with particular emphasis placed on the calculation of the high-frequency elements in the paramagnetic part of the susceptibility. The results are in good agreement with a recently observed susceptibility value and suggests that a previously proposed MO scheme is consistent in accounting for the magnetic properties of the molecule. A small ring current was also calculated, thus substantiating the delocalized MO description advanced by others.

64-14. Boudreaux, Edward A.

ELECTRONIC STRUCTURE AND SPECTRUM OF XeF_4 , *J. Chem. Phys.* **40**, 246-7 (1964).

Standard group-theoretical methods were used in deriving various molecular-orbital combinations for XeF_4 . Spectral characteristics ascribed to symmetry-allowed singlet-singlet transitions are given. The effective charge on Xe in XeF_4 was computed to be 0.412, and is in good agreement with that inferred from NMR data. The ionization potential (13.2 eV) estimated from the data also seems reasonable.

64-15. Brown, George M., and Henri A. Levy

RECENT CRYSTAL STRUCTURE DETERMINATIONS BY NEUTRON DIFFRACTION AT OAK RIDGE, *J. Phys.* **25**, 469-73 (1964).

Crystal structures were determined from three-dimensional neutron data for xenon difluoride, xenon tetrafluoride, barium chloride dihydrate, potassium heptafluorobate, chloral hydrate, sucrose, and strontium hydroxide octahydrate. Data were taken on the automatic three-circle neutron diffractometer. Refinements, by the method of least squares, yielded structural parameters of high precision.

64-16. Brown, Thomas H., Paul H. Kasai, and Peter H. Verdier

ANOMALIES IN THE NMR AND EPR SPECTRA OF XeF_4 -HF MIXTURES, *J. Chem. Phys.* **40**, 3448-9 (1964).

A single broad line with $T_2 < T_1$ was previously observed in the ^{19}F NMR spectrum of XeF_4 in HF. The width and shift of the line depend upon the XeF_4 concentration, while the width is independent of the magnetic field. $T_2 < T_1$ indicates line broadening due to chemical exchange. It appears that a third species with appreciable ^{19}F shift is involved in the ^{19}F exchange. The presence of a third species was confirmed by observation of a resolved EPR spectrum after most of the HF had evaporated. The experimental results can be explained in terms of a paramagnetic contaminant or a low-lying triplet electronic state in XeF_6 .

64-17. Brown, T. H., and P. H. Verdier

KRYPTON TETRAFLUORIDE: ^{19}F HIGH RESOLUTION MAGNETIC RESONANCE SPECTRUM, *J. Chem. Phys.* **40**, 2057 (1964).

The ^{19}F high-resolution magnetic resonance spectrum of KrF_4 in HF shows a fluorine chemical shift of -254 ppm relative to HF.

64-18. C  zaire, Jean

INERT GASES WHICH ARE NOT INERT, AT LEAST WITH FLUORINE, *Nature (Paris)* No. 3346, 53-8 (1964) (In French).

A short review, giving some historical reasons for believing the gases to be inert.

64-19. Chernick, Cedric L.

THE NOBLE GAS COMPOUNDS, *Chemistry* **37**, 6-12 (1964).

The history and developments in the synthesis of rare gas compounds are reviewed. The nature of bonding is also discussed.

64-20. Chernick, Cedric L.

"COMPOUNDS"(?) OF THE NOBLE GASES PRIOR TO 1962, *J. Chem. Educ.* **41**, 185-6 (1964).

A brief review is presented on developments in rare gas compounds prior to 1962. The developments consisted primarily of predictions. Despite much hard and exhaustive work, the position early in 1962 was that no unrefutable proof had been given for the existence of a compound in which a noble gas was chemically bond to another entity. He, Ne, Ar, Kr, Xe, and Rn were considered inert gases.

64-21. Claassen, Howard, H., and Geraldine Knapp

RAMAN SPECTRUM OF XENIC ACID, *J. Am. Chem. Soc.* **86**, 2341-2 (1964).

The Raman spectrum of a 2.0 M aqueous solution of XeO_3 was obtained. Intense bands at 780, 344, 833, and 317 cm^{-1} were assigned as ν_1 , ν_2 , ν_3 , and ν_4 , respectively, of unionized XeO_3 molecules of symmetry C_{3v} . Several much weaker bands were assigned to a low concentration of an unknown species.

64-22. Clifford, A. F., and G. R. Zeilenga

XENON FLUOROSILICATE AND RELATED COMPOUNDS, *Science* **143**, 1431 (1964).

The reaction product of Xe, F_2 , and SiF_4 in a glow discharge is shown to have a composition approximating Xe_2SiF_6 . It and a similar hexafluorophosphate are unstable at room temperature. A stable hexafluoroantimonate is formed from Xe, F_2 , and SbF_5 at 250°C .

64-23. Coulson, C. A.

THE NATURE OF THE BONDING IN XENON FLUORIDES AND RELATED MOLECULES, *J. Chem. Soc.*, 1442-5 (1964).

A survey is given of four distinct theories that have been proposed to describe the bonding in fluorine compounds of xenon and related molecules. It is shown that a valence-bond resonance picture is the simplest

satisfactory description, but a molecular-orbital picture may also be used and is of great value in characterizing the various possible electronic transitions. Further, an explicit relation is obtained between the wave functions corresponding to the two models. The significance both of the large size and low ionization potential of the central (heavy) atom, and of the small size and high electronegativity of the ligand atoms, is stressed.

64-24. Falconer, W. E., J. R. Morton, and A. G. Streng

ELECTRON SPIN RESONANCE SPECTRUM OF KrF , *J. Chem. Phys.* **41**, 902-3 (1964).

The trapped radical KrF was produced by γ irradiation of a single crystal of KrF_4 . The ESR spectrum at 77°K was examined and the results compared with those obtained with XeF . The spin population in the $2s$ and $2p_z$ F orbitals is higher in KrF than in XeF . This is consistent with the higher Kr electronegativity, compared with Xe, which results in lower fluorine character in the KrF bonding orbitals.

64-25. Feltz, Adalbert

THE VALENCE COMPOUNDS OF INERT GASES, *Z. Chem.* **4**(2), 41-9 (1964) (In German).

A general review of noble gas compound chemistry. 61 references.

64-26. Ferreira, Ricardo

THE RELATIVE STABILITIES OF NOBLE GAS COMPOUNDS, *Inorg. Chem.* **3**, 1803-4 (1964).

It is shown that chemical evidence suggests that some argon compounds may be more stable than the corresponding compounds of krypton and, therefore, that there is a fair prospect of coaxing argon into forming relatively stable compounds. The oxygen compounds of argon are expected to be more stable than corresponding krypton compounds.

64-27. Gard, Gary Lee

STUDIES IN FLUORINE CHEMISTRY: I. SOME FLUORINE CONTAINING COMPOUNDS OF XENON. II. THE ROLE OF WATER IN THE SYNTHESIS OF TRIFLUOROACETYL HYPOFLUORITE, Thesis, Seattle, Univ. of Washington, 1964. 84p.

XeF_2 was shown to react with water, giving xenon, oxygen, and HF . In the presence of KI, iodine is liberated. With SO_3 only fluorination occurs, liberating free xenon. XeF_6 reacts with water to give xenic acid, with HCl to give chlorine, and with perfluorocyclopentene to give perfluorocyclopentane. It also reacts with SbF_5 to give solid adducts ($\text{XeF}_6 \cdot \text{SbF}_5$, $\text{XeF}_6 \cdot 2\text{SbF}_5$, and $2\text{XeF}_6 \cdot \text{SbF}_5$). These adducts were characterized by their physical properties and powder spectra. Proof for these adducts was obtained both by analysis and synthesis. In a study of the role of water vapor in allowing trifluoroacetyl hypofluorite to be formed by the reaction of fluorine with trifluoroacetic acid vapor, it was found that the yield of the hypofluorite was negligible when water was absent and that increasing the amount of water vapor up to a certain limit caused an increase in the yield of the hypofluorite. Above this limit, additional water appeared to have no influence on the yield. It appears likely that the role of water in the

reaction is to form a reactive intermediate by reaction with fluorine or trifluoroacetic acid. Attempts to prepare a "solid hypofluorite" with SbF_5 were unsuccessful, but a convenient preparation of SF_5OF and SF_5OOSF_5 was developed. Peroxydisulfuryl difluoride was found to act as a fluorinating agent and possibly as an oxygenating-fluorinating reagent.

64-28. Gard, Gary L., and George H. Cady

REACTIONS OF XENON HEXAFLUORIDE WITH ANTIMONY PENTAFLUORIDE, HYDROGEN CHLORIDE, AMMONIA, AND PERFLUOROCYCLOPENTENE, *Inorg. Chem.* **3**, 1745-7 (1964).

By varying the proportions of the reactants, SbF_5 and XeF_6 , it was possible to prepare each of the crystalline solids: $\text{XeF}_6 \cdot 2\text{SbF}_5$, $\text{XeF}_6 \cdot \text{SbF}_5$, $\text{SbF}_5 \cdot 2\text{XeF}_6$, HCl , NH_3 , and perfluorocyclopentene reacted readily with XeF_6 , but the products were not found to include substances in which xenon is in combination with chlorine, nitrogen, and carbon, respectively.

64-29. Gellings, P. J.

BOND LENGTHS IN XENON (II) FLUORIDE, *Z. Physik. Chem. (Frankfurt)* **43**, 123-5 (1964).

In considering the 110 plane of the XeF_2 unit cell, three forces to which one fluorine atom is subjected were analyzed to explain the increase in Xe-F bond lengths upon solidification. The downward force due to repulsion by another fluorine atom, the downward force due to attraction by a xenon atom, and an upward force due to another fluorine atom would account for an increase of about 10% in the Xe-F distance upon solidification. Polarization of the F atoms and increase of coordination number with resulting increase in atomic distances made smaller contributions to the increased distance in the solid. The direct electrostatic interaction was the primary cause of the increased distance. The same forces resulted in the similar but smaller Xe-F distances in XeF_4 .

64-30. Greenwood, N. N.

CHEMISTRY OF THE NOBLE GASES, *Educ. Chem.* **1**(4), 176-88 (1964).

General review of chemistry, together with a discussion of stability and nature of bonding.

64-31. Holloway, J. H.

REACTIONS OF THE NOBLE GASES, *Progr. Inorg. Chem.* **6**, 241 (1964).

Review with 98 references.

64-32. Hoppe, R.

THE VALENCE COMPOUNDS OF THE NOBLE GASES, *Angew. Chem. Intern. Ed.* **3**, 538 (1964). [Original Paper in German, *Angew. Chem.* **76**, 455-63 (1964).]

A review with 121 references is presented. In the introduction, note is given to molecules containing He which exist in excited states, and to rare gas hydrates, rare gas double hydrates (containing an organic compound as the second species in water), and cage compounds with hydroquinone. Earlier attempts and investigations are discussed. The first preparation of noble gas fluorides is discussed, with the question of priority

for the German group under Hoppe against that for the American group under Claassen being raised; a brief history of the German effort is included. A short section on preparation of noble gas compounds is given. Particular detail is given to the preparation, chemical and physical properties, and reactions of XeF_2 and XeF_4 . The chemistry of the higher fluorides and oxyfluorides of Xe is outlined, together with that of the fluorides of Kr, fluorine compounds of higher order, and oxygen compounds of Xe. A section on the thermochemistry of these compounds and on bond properties is included, and a general discussion of progress in the field completes the article.

64-33. Huston, John L., Martin H. Studier, and Eric N. Sloth

XENON TETROXIDE: MASS SPECTRUM, *Science* **143**, 1161-2 (1964).

The spectrum of XeO_4 is reported. The typical isotope pattern of Xe is repeated every 16 mass units up to XeO_4 . The exact mass of the tetroxide was verified further by reference to the spectrum of Hg. The fragmentation pattern varied very little with the energy of the ionizing beam of electrons. The volatility of XeO_4 was demonstrated by its very rapid distillation when a liquid nitrogen bath was replaced by one of dry ice.

64-34. Hyman, Herbert H.

THE CHEMISTRY OF THE NOBLE GASES, *J. Chem. Educ.* **41**, 174-82 (1964).

The chemistry of the rare gases is discussed, along with theoretical approaches currently used to explain chemical bond formation, and the course of developments in rare gas chemistry are reviewed for the year 1963.

64-35. Hyman, H. H.

THE CHEMISTRY OF NOBLE GAS COMPOUNDS, *Science* **145**, 773-83 (1964).

The synthesis of simple fluorides, oxyfluorides, oxides, and xenates and perxenates is reviewed. Special attention is given to xenon compounds. 72 references are included.

64-36. Ibers, James A., Walter C. Hamilton, and D. R. MacKenzie

THE CRYSTAL STRUCTURE OF SODIUM PERXENATE OCTAHYDRATE, *Inorg. Chem.* **3**, 1412-16 (1964).

Sodium perxenate octahydrate, $\text{Na}_4\text{XeO}_6 \cdot 8\text{H}_2\text{O}$, is orthorhombic with cell constants $a = 11.86$, $b = 10.6$, and $c = 10.43$ Å, belonging to space group Pbcn , $Z = 4$. A three-dimensional X-ray diffraction investigation resulted in a complete structure determination. The perxenate ion is approximately a regular octahedron with a mean Xe-O distance of 1.864 ± 0.012 Å. The greatest deviation of an O-Xe-O angle from the ideal 90° is $2.6 \pm 0.8^\circ$. The two crystallographically independent sodium atoms are surrounded by very distorted octahedra composed of water molecules and perxenate oxygen atoms. A complex array of hydrogen bonds completes the structure.

64-37. Israël, Julius

TENTATIVE INTERPRETATION OF THE ULTRAVIOLET SPECTRUM OF XENON DIFLUORIDE, *Bull. Soc. Chim. France*, 649 (1964) (In French).

The ultraviolet spectrum of XeF_2 is explained on the basis of a model proposed by Walsh (*J. Chem. Soc.*, 2266 (1953)).

64-38. Israël, Julius

TENTATIVE INTERPRETATION OF THE ULTRAVIOLET SPECTRUM OF XENON TETRAFLUORIDE, *Bull. Soc. Chim. France*, 649-50 (1964) (In French).

An explanation of the ultraviolet spectrum of XeF_4 is presented.

64-39. Jameson, Cynthia Juan, and H. S. Gutowsky

CALCULATION OF CHEMICAL SHIFTS. II. THE XENON FLUORIDES, *J. Chem. Phys.* **40**, 2285-93 (1964).

Xenon chemical shifts in XeF_2 , XeF_4 , XeF_6 , and XeOF_4 were calculated by means of the general methods previously presented. Comparisons with the experimental chemical shifts show that the change in $\sigma^{(2)}$, the paramagnetic contribution, is the dominant term and that a localized description using spd-hybrid xenon orbitals gives better agreement with experiment than a delocalized MO description using no d hybridization. In addition, the indirect Xe-F and Xe-O coupling constants observed in XeF_2 , XeF_4 , and XeOF_4 are more consistent with the localized models. The fluorine chemical shifts were used to estimate the ionicity of the Xe-F bonds. Also, a comparison of the anisotropy predicted for the fluorine shift in XeF_4 with an experimental value shows that the fluorine shifts result almost entirely from differences in $\sigma^{(2)}$.

64-40. Jaselskis, Bruno

XENIC ACID: REDUCTION AT THE DROPPING MERCURY ELECTRODE, *Science* **143**, 1324 (1964).

Xenic acid is reduced at the dropping-mercury electrode in a single step to xenon. The half-wave potential for the reduction of xenic acid changes from approximately -0.10 to -0.360 V against a saturated Hg_2SO_4 -Hg reference electrode in the pH range 4.60 to 8.00. The diffusion current varies linearly with concentration of xenic acid.

64-41. Jaselskis, Bruno

SODIUM PERXENATE AND XENON (II) DIFLUORIDE REDUCTION AT THE DROPPING-MERCURY ELECTRODE, *Science* **146**, 263-4 (1964).

Sodium perxenate in alkaline solutions was reduced in a single step to xenon at the dropping-mercury electrode. The half-wave potential for perxenate changes from -0.21 to -0.31 V against a Hg_2SO_4 -Hg reference electrode in the pH range 10.1 to 11.3. XeF_2 in acidic solutions was reduced in a single step to xenon at the potential of approximately zero against the Hg_2SO_4 -Hg reference electrode. The reduction wave was followed by a broad maximum that can be effectively suppressed by fluoride ion. The diffusion current varies in linear fashion with concentration.

64-42. Jaselskis, Bruno, and Stanislaus Vas

XENIC ACID REACTIONS WITH VIC-DIOLS, J. Am. Chem. Soc. **86**, 2078-9 (1964).

Results are reported of qualitative studies of reactions of xenic acid with vic-diols and primary alcohols. Reactions to yield xenon gas and carbon dioxide or carboxylic acids take place readily in neutral or basic solution, but are not observed in acid solution.

64-43. Johnston, Harold S., and Robert Woolfolk

REACTION RATES OF XENON FLUORIDES WITH OXIDES OF NITROGEN, J. Chem. Phys. **41**, 269-73 (1964).

The rate of reaction of XeF_4 and XeF_2 with NO and with NO_2 was studied between 300 and 250°K at pressures between 0.1 and 30 mm. The second-order rate constant at 300°K and the activation energies are, respectively: $\text{XeF}_4 + \text{NO}$, 3 liters/mole-sec, 7 kcal/mole; and $\text{XeF}_2 + \text{NO}$, 0.3 liters/mole-sec, 10 kcal/mole. The rate of NO_2 with XeF_4 and XeF_2 was too slow to observe: $k < 0.01$ liter/mole-sec. The fluorides of xenon react with the oxides of nitrogen much more slowly than F_2 reacts with NO or NO_2 . By means of a Polanyi-Semenov plot, the reactions of XeF_4 , XeF_2 , and F_2 with oxides of nitrogen were combined to give an estimate of the successive dissociation energies of XeF_n , which are (in kcal/mole): $\text{XeF}_4 \rightarrow \text{XeF}_3 + \text{F}$, 48; $\text{XeF}_3 \rightarrow \text{XeF}_2 + \text{F}$, 15; $\text{XeF}_2 \rightarrow \text{XeF} + \text{F}$, 54; $\text{XeF} \rightarrow \text{Xe} + \text{F}$, 11. From these kinetic and thermochemical data a strong case could be made for the stepwise reduction of XeF_4 .

64-44. Karplus, M., C. W. Kern, and D. Lazdins

SHIELDING ANISOTROPIES IN XENON FLUORIDES, J. Chem. Phys. **40**, 3738-9 (1964).

An analysis was made to determine whether the anisotropy measurement in consistent with a theoretical model that has been proposed for the chemical shifts of fluorine and xenon in xenon fluorides. From the theoretical results, the sign of the shielding anisotropy of ^{135}F in XeF_4 was determined.

64-45. Kaufman, Joyce J.

BONDING IN XENON HEXAFLUORIDE, J. Chem. Educ. **41**, 183-4 (1964).

The theory of bonding in XeF_2 and XeF_4 is discussed. The distinguishing difference is that one group favors Xe 5d-orbital hybridization with its 5s and 5p orbitals; the other favors bonds involving primarily only the Xe 5p orbitals. Both hybridization or nonhybridization of Xe and 5s and 5d orbitals with Xe 5p orbitals appear to predict correctly a linear structure for XeF_2 and a square planar structure for XeF_4 . The inclusion of Xe 5d-orbital hybridization would seem to indicate for XeF_4 two possible structures, a pentagonal pyramid or an irregular octahedron (both based on fragments of a pentagonal bipyramid in which one vertex is unoccupied). These structures would arise from consideration of the most stable arrangement of seven electron pairs (whether bonded or nonbonded) around a central atom in sp^3d^3 ($\text{sp}^3\text{d}_2^2\text{d}_z$) hybridization. However, there is a structural possibility for XeF_6 , alternative to these two forms, involving only partial Xe 5d-orbital hybridization which could lead to an octahedral XeF_6 structure in

the following manner. The Xe atom is in sp^3d^2 ($\text{sp}^3\text{d}_2^2\text{d}_{x^2-y^2}$) hybridization which would place the F atoms symmetrically around the Xe at the vertices of an octahedron, while the extra long-pair of electrons remains on the Xe in an unhybridized d_z orbital. It is pointed out that when invoking the separated electron-pair valence-bond method that, under certain special conditions, it is possible to have nonparticipation in valence-shell hybridization of d orbitals which contain one or a pair of essentially nonbonding electrons. The other theoretical assumption using only the Xe 5p orbitals would lead to an octahedral structure for XeF_6 . It is concluded that while a XeF_6 structure based on a pentagonal bipyramidal or distorted octahedral fragment would be conclusive evidence for Xe 5d-orbital participation, an octahedral XeF_6 structure should not be construed as conclusive evidence favoring either Xe 5d-orbital participation or the lack of it.

64-46. Khutoretskii, V. M., and V. A. Shpanskii

THE REACTIVITY OF NOBLE GASES. A NEW METHOD OF PREPARING XeF_2 , Doklady Akad. Nauk SSSR **155**, 379-80 (1964) (In Russian).

Most of the methods of preparing various xenon fluorides require a high temperature and pressure, and an excess of fluorine. It is shown that XeF_2 can be formed from its element with the use of pressure at room temperature with the evolution of heat (a very preliminary value for the reaction heat is 40 to 60 kcal/mol). Sometimes an explosion takes place. A vessel with a volume of 80 ml was pressurized with F_2 to 18 atm (2.17 g), and then xenon was introduced to a pressure of 35 atm (6.81 g). The pressure immediately increased, and then fell to 8 atm. A residue of 6.70 g of a solid remained after removing the unreacted gases. Hydrolysis of the residue with 0.1N NaOH showed that the sample was XeF_2 . The reaction proceeded more gradually in a vessel with a volume of 30 ml. The pressure decreased by a factor of two over a period of a few days. The reaction rate became insignificant at a pressure of 8 to 12 atm. It was concluded that it may be possible to synthesize compounds such as XeCl_2 , XeO , and KrF_2 under these conditions.

64-47. Koch, Charles W., and Stanley M. Williamson

A STUDY OF THE STABILITY OF XENON TRIOXIDE IN BASIC SOLUTIONS, J. Am. Chem. Soc. **86**, 5439-44 (1964).

The reaction of $\text{XeO}_3(\text{aq})$ with NaOH and KOH solutions in the range of 0.25 to 4.2 M and 2.0 to 3.6 M, respectively, at room temperature gave a 33% yield of the alkali perxenate. Higher $[\text{OH}^-]$ and temperature increase the yield. Lowering the $[\text{OH}^-]$ toward the neutral point led to the direct decomposition of XeO_3 . For comparable concentrations for LiOH, the yield of perxenate was 50% and higher. A yellow, mixed oxidation-state complex with variable stoichiometry formed predominantly in the NaOH and KOH systems. It provided a mechanism by which Xe(VI) directly decomposed to $\text{Xe} + 1.5\text{O}_2$. In the KOH system, the complex was present as a solid during most of the course of the reaction. Subsequently, $\text{K}_4\text{XeO}_6 \cdot 9\text{H}_2\text{O}$ was isolated. The relative stabilities of the alkali and alkaline earth perxenates, a mechanism for the

disproportionation-decomposition reaction of XeO_3 , and the nature of the mixed oxidation-state complex are presented.

64-48. Lavrovskaya, G. K., V. E. Skurat, and V. L. Tal'roze

THE RADIATION SYNTHESIS OF THE XENON FLUORIDES, Dokl. Akad. Nauk SSSR 154, 1160-2 (1964) (In Russian).

The syntheses of XeF_2 and XeF_4 were carried out in a stainless steel reactor by irradiating a mixture of xenon and fluorine with 1.6-MeV electrons on cooling the reactor to liquid air temperatures. A total of 30 to 50% of the xenon reacted to form XeF_2 and XeF_4 , which were identified by their infrared spectra. Significant absorption was observed at wavelengths of 565 cm^{-1} (corresponding to absorption by XeF_2), and less absorption was observed at 584 cm^{-1} (corresponding to absorption by XeF_4). A control experiment where fluorine was placed in the reactor without xenon showed no infrared absorption at 565, 550, and 584 cm^{-1} . Thus, these results show that XeF_2 and XeF_4 were obtained by radiation synthesis. If the G yield of hydrogen from the irradiation of methane was assumed to be 5.6 molecules per 100 eV of absorbed dose, the radiation yield for the disappearance of xenon was found to be 0.4 to 0.7 molecules per 100 eV of absorbed dose. This value was valid only for large doses.

64-49

PHYSICAL CHEMISTRY (Univ. of California, Berkeley. Lawrence Radiation Lab.), pp. 87-138 in UCRL-11213, 1964.

The topics studied include: activation analysis for C and N, Cm metal, ThI_4 , TbCl_3 , $\text{HgSO}_4 \cdot \text{H}_2\text{O}$, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, XeO_3 , $\text{Na}_4\text{XeO}_6 \cdot 6\text{H}_2\text{O}$, XeF_4 , ion exchange of alkaline earth cations, extraction of HAuCl_4 and HAuBr_4 , large univalent ions, radioinduced reactions of poly-L-glutamic acid and alanine, CO_2 ions, organic mass spectra, triple ionization, molecular-beam electric resonance in alkali metal halides, Am(IV) in LaCl_3 , luminescence of Bk^{3+} , analysis of atomic spectra, 1^N configurations, quadrupole antishielding in rare earths, isomer shifts, conversion electrons from oriented ^{137}mCe , polarization of Ag nuclei in Fe and Ni, ^{171}Er , and chemistry of $^{34}\text{S}(\text{n}, \gamma)$ reactions in gaseous S compounds.

64-50. Martins, Joseph, and E. Bright Wilson

MICROWAVE SPECTRUM OF XENON OXYTETRAFLUORIDE, J. Chem. Phys. 41, 570-1 (1964).

The microwave spectrum of XeOF_4 was investigated at 20 to 40 Bc with a conventional Stark modulated spectrometer to determine structure parameters. Transitions were observed for five naturally occurring isotopes of xenon in the ^{16}O species and for two of these isotopes in an ^{18}O -enriched sample. From the rotational constants of the various isotopic species the structural parameters, based on a C_{4v} model, were calculated. Because the xenon atom lies $0.1 \pm 0.03\text{ \AA}$ from the center of mass of the molecule, the uncertainty in its location is relatively large and introduces large uncertainties in the rest of the structure.

64-51. Mellor, D. P.

THE CHEMISTRY OF XENON, Proc. Roy. Aust. Chem. Inst. 31, 85-90 (1964).

A short review of the discovery of the noble gases, early attempts to prepare compounds, and the preparation and properties of xenon and krypton compounds.

64-52. Mukherjee, Asok Kumar

THE CHEMISTRY OF NOBLE GASES, J. Sci. Ind. Res. 23, 103-5 (1964).

A brief review is presented on the discovery, methods of preparation, chemical properties, electronic theories of bonding, and structure of compounds of rare gases. Special attention is given to xenon fluorides.

64-53. Nagarajan, G.

MEAN AMPLITUDES OF VIBRATION AND THERMODYNAMIC FUNCTIONS OF XENON TETRAFLUORIDE, Acta Phys. Austriaca, 18: 11-19 (1964).

The vibrational and molecular structural analyses for XeF_4 possessing a square planar configuration with the symmetry point group D_{4h} are comprehensively reported. The mean amplitudes of vibration at the temperatures $T = 0$ and $T = 298^\circ\text{K}$ were studied after evaluating the force constants. The molar thermodynamic functions were also calculated on the basis of a rigid-rotator, harmonic-oscillator approximation for the temperature range from 50 to 2000°K .

64-54. Nagarajan, G.

MEAN AMPLITUDES OF VIBRATION AND THERMODYNAMIC FUNCTIONS OF THE TRIOXIDES OF XENON AND RHENIUM, Bull. Soc. Chim. Belges 73, 655-72 (1964).

The mean amplitudes of vibration for trioxides of Xe and Re possessing a pyramidal structure with the symmetry point group C_{3v} have been evaluated on the basis of the principle postulated by Cyvin at 0 and 298°K , respectively. The molar thermodynamic functions also have been calculated for these molecules with an assumption of a rigid-rotor, harmonic-oscillator model for the temperature range $100\text{--}2000^\circ\text{K}$.

64-55

CHEMICAL PHYSICS, pp. 94-116 in ORNL-3679, 1964.

A progress report covering work on many problems. ...Analysis of three-dimensional X-ray precession data of a crystalline material grown from XeF_6 preparations yielded the monoclinic space group $\text{P2}_1/\text{m}$, with eight Xe atoms per unit cell. A Patterson synthesis placed these into two regular tetrahedral groups, related by a center of symmetry. A length of $4.19 \pm 0.02\text{ \AA}$ for the edges of the Xe tetrahedra was obtained. Molecular-beam scattering techniques were used to study intermolecular potentials and chemical reactions in a number of systems. Rainbow scattering was observed in the K-Xe system, and the depth of the interatomic potential well was found to be 200 cal. Measurement of the relative total cross section of scattering of K by I_2 and by atomic I indicated that the contribution of electronic exchange to the potential was observable in the total scattering cross section...

CHEMICAL SEPARATION OF ISOTOPES, pp. 21-41 in ORNL-3488, 1964.

A progress report covering work on many problems. ...NMR chemical shifts were measured for liquid XeF_3 , XeF_4 , XeOF_4 , and XeF_6 , and ^{19}F - ^{129}Xe spin-spin coupling constants for XeF_4 and XeOF_4The Raman spectra of solid XeF_2 , gaseous XeF_2 , solid XeF_4 , solid XeF_6 , and liquid XeOF_4 were observed and assignments made of the observed bands.

64-57

ISOTOPE CHEMISTRY, pp. 23-38 in ORNL-3679, 1964.

A progress report covering work on many problems. ...The infrared and Raman spectra of the square pyramidal molecules XeOF_4 , IF_5 , BrF_5 , and ClF_3 were recorded, and valence force constants were calculated. The remarkable resemblance between the Xe compound and the interhalogen compounds is pointed out. ...

64-58

MATERIALS STUDIES, pp. 71-143 in ORNL-3529, 1964.

Progress made in the development of fuels, coolants, and reactor materials for the Molten Salt Reactor Experiment is reported. Properties and structure of the materials are described along with the effects of radiation and fabrication techniques on the materials. The development of equipment and processes is investigated for the molten fuels and coolants. Analytical methods and tests are outlined.

64-59. Peacock, R. D., and J. H. Holloway

NEW NOBLE GAS COMPOUNDS, Sci. Progr. (London) 52, 42-9 (1964).

A review is presented on the synthesis of rare gas compounds, with special attention given to xenon compounds. The physical properties of xenon fluorides and oxides are given. Reactions of xenon fluorides are also shown. 26 references.

64-60. Peacock, R. D., H. Selig, and I. Sheft

COMPLEX FLUOROXENATES(VI), Proc. Chem. Soc., 285 (Sept 1964).

The preparation of complexes between xenon hexafluoride and the alkali fluorides is discussed. The preparation and properties of xenon fluoride complexes with cesium and rubidium fluorides are described. Rubidium and cesium octafluoroxenate are the most stable solid xenon compounds yet known.

64-61. Perlow, Gilbert J.

RATIO OF THE QUADRUPOLE MOMENT OF THE FIRST EXCITED STATE OF ^{129}Xe TO THAT OF THE GROUND STATE OF ^{131}Xe , Phys. Rev. 135, B1102-5 (1964).

The Mössbauer effect for ^{129}Xe and ^{131}Xe contained in XeF_4 was used to measure the ratio of electric quadrupole moments of the lowest $3/2^+$ states in the two isotopes. This is the ground state in ^{131}Xe and the first excited state in ^{129}Xe . The value $Q(^{129}\text{Xe})/Q(^{131}\text{Xe}) = 3.45 \pm 0.09$ is obtained. The sign of the moment in ^{129}Xe is obtained by use of a source containing

oriented crystals of $\text{K}^{129}\text{ICl}_4$ which produces XeCl_4 in its beta decay. The quadrupole moment is found to be negative. The known quadrupole moment of the ground state of ^{131}Xe , -0.12b, then gives $Q(^{129}\text{Xe}) = -0.41\text{b}$. The large ratio of the moments is interpreted as due to the abrupt onset of a region of permanent deformation by analogy with a similar situation in the europium isotopes. Discussions of such a region appear in the literature. The linewidth observed in ^{131}Xe yields a value for the first-excited-state lifetime, $T_{1/2} = 0.504 \pm 0.017$ nsec, in good agreement with delayed-coincidence measurements. The measured value for the ratio of the moments removes a difficulty in understanding the structure of xenon fluorides generated by an earlier assumption that the ratio was unity.

64-62. Perlow, G. J., and M. R. Perlow

MÖSSBAUER EFFECT EVIDENCE FOR THE EXISTENCE AND STRUCTURE OF XeCl_4 , J. Chem. Phys. 41, 1157-8 (1964).

Evidence for the existence of XeCl_4 is presented, and a measurement of quadrupole coupling, which connects its structure with that of the square planar substances XeF_4 and ICl_4^- , is described. The technique used was the Mössbauer effect of the 40-keV gamma ray emitted in the transition from the first excited state to the ground state of ^{129}Xe , following the beta decay of ^{129}I .

64-63. Perlow, G. J., and M. R. Perlow

THE MÖSSBAUER EFFECT IN XENON COMPOUNDS, Rev. Mod. Phys. 36, 353-57 (1964).

Studies were made of the structure of Xe compounds using the Mössbauer effect. In the first experiments, XeF_2 , XeF_4 , hydroquinone-Xe clathrate, and a perxenite of nominal composition $\text{Na}_4\text{XeO}_6 \cdot \text{H}_2\text{O}$ were used as absorbers, with Na^{129}I as the source. No isomer shift outside the experimental error was observed; the clathrate and xenite show single lines while the fluorides show quite large quadrupole splitting. Similar experiments using $^{131}\text{XeF}_4$ and Na^{131}I as absorber and source, respectively, showed no absorption dips. Next, several ^{129}I sources (I_2 , NaI , NaIO_3 , and $\text{Na}_2\text{H}_2\text{IO}_6$) were studied with Xe clathrate as absorber; the line width was found to be the same for all sources. The results are interpreted in terms of XeO_3^+ and XeO_4^- ions.

64-64. Perlow, G. J., and M. R. Perlow

PRODUCTION OF XENON COMPOUNDS BY THE BETA DECAY OF IODINE IN IODINE COMPOUNDS, Vienna, International Atomic Energy Agency, 1964, Preprint SM-57/83, 27p. (CONF-773-10). (See 65-41.)

From Symposium on Chemical Effects Associated with Nuclear Reactions and Radioactive Transformation, Vienna, Dec 1964.

Beta decay ^{129}I - ^{129}Xe in an iodine compound was studied by use of the Mössbauer effect for ^{129}Xe . In the first experiments a source of Na^{129}I was used with absorbers of hydroquinone clathrate, Na_4XeO_6 , XeF_4 , and XeF_2 . Single-line spectra were observed for the clathrate and perxenite and two-line spectra for the fluorides. The single line indicates that in the source $\text{I}^- \rightarrow \text{Xe}^0$, its iso-electronic daughter. When $\text{Na}_2\text{H}_2\text{IO}_6$ was used as source, with clathrate absorber, the recoilless fraction increased by a factor of 3, implying stronger bonding. KIO_4 also gave a single but somewhat less

intense line. With NaIO_3 as source and clathrate absorber, splitting was observed suggesting that $\text{IO}_3^- \rightarrow \text{XeO}_3$. This was verified by the observation of identical splitting in an XeO_3 absorber used with KIO_4 source. An experiment with $\text{KICl}_4 \cdot \text{H}_2\text{O}$ as source and clathrate absorber showed splitting somewhat smaller than in XeF_4 . Here $\text{ICl}_4^- \rightarrow \text{XeCl}_4$. Using aligned crystals of $\text{KICl}_4 \cdot \text{H}_2\text{O}$ and making quantitative intensity measurements, it was established that the square planar structure of ICl_4^- is preserved in the transition to XeCl_4 , and that XeCl_2 and Xe^0 are not formed in the reaction in detectable amounts. With $\text{Na}_2\text{H}_2^{131}\text{IO}_6$ as source, the effect was observed in ^{131}Xe . Comparing XeF_4 spectra in both isotopes calibrated the splitting in ^{129}Xe and enabled quantitative comparison of XeF_4 and XeCl_4 with ICl_4^- , and of XeO_3 with IO_3^- . The unsplit KIO_4 spectrum implies that the tetrahedral ligand environment of the iodine is preserved in the resulting XeO_4 . Similarly, the paraperiodate result is consistent with preservation of its octahedral environment.

64-65. Pimentel, George C., Richard D. Spratley, and Alan R. Miller

HELIUM DIFLUORIDE: POSSIBLE PREPARATIVE TECHNIQUES BASED ON NUCLEAR TRANSMUTATIONS, *Science* **143**, 674 (1964).

Difluoride may be prepared by beta decay of tritium, lithium-6 transmutation, or alpha-particle bombardment. In the first method, which may be the most feasible, tritiated potassium bifluoride could be used as a host lattice. The beta-decay recoil energy would not dislodge the daughter helium atom from the host site, thus helium difluoride could perhaps be formed in an ideally shaped lattice site.

64-66. Pysh, Eugene S., Joshua Jortner, and Stuart A. Rice

FORBIDDEN ELECTRONIC TRANSITIONS IN XeF_2 AND XeF_4 , *J. Chem. Phys.* **40**, 2018-32 (1964).

Transition strengths were measured for the weak 2330-Å band in XeF_2 ($f = 0.002$) and for the two weak bands in XeF_4 at 2280 Å ($f = 0.009$) and 2580 Å ($f = 0.003$). To investigate the origins of these weak transitions, the possibilities of vibronic and singlet-triplet transitions in XeF_2 and XeF_4 were examined. By means of the Herzberg-Teller theory of vibronic transitions and a molecular-orbital treatment of excited electronic states, estimated strengths of the relevant vibronic transitions were calculated to be $f = 0.001$ for both XeF_2 and XeF_4 . The vibronic band in XeF_2 borrows intensity from the symmetry-allowed $^1\text{A}_{1g} \rightarrow ^1\text{A}_{2u}$ transition at 1580 Å ($f = 0.45$), whereas in XeF_4 the major contribution to the vibronic band is from the symmetry-allowed $^1\text{A}_{1g} \rightarrow ^1\text{E}_u$ transition at 1325 Å ($f = 0.8$). A temperature dependence of the intensity of the 2330-Å band in XeF_2 was observed and found to be less than that predicted by the Herzberg-Teller theory. The estimated strength of the singlet-triplet transition in XeF_2 corresponding to the singlet-singlet transition at 1580 Å is shown to be small ($f \leq 10^{-4}$) in spite of a heavy-atom effect; the small transition strength persists because of the lack of nearby excited states of the required symmetry. In XeF_4 , the triplet excited state $^3\text{E}_u$ corresponding to the singlet-singlet transition $^1\text{A}_{1g} \rightarrow ^1\text{E}_u$ at 1840 Å ($f = 0.22$) is permitted by group-theoretical selection rules to mix

with its own singlet state. By use of an intermediate coupling scheme the estimated intensity of this singlet-singlet transition was calculated to be $f = 0.07$. The theoretical estimates of the symmetry and spin-forbidden transition strengths were used for the assignment of the weak electronic transitions in the xenon fluorides.

64-67. Schroth, Francis, and Jean-Pierre Adloff

THE SZILARD-CHALMERS EFFECT ON XENON TETRAFLUORIDE, *Compt. Rend.* **258**, 5863-5 (1964). (In French.)

The retention of the radioactive isotopes of xenon in xenon tetrafluoride irradiated in the solid state by neutrons is, on an average, 60%. During the acid or alkaline hydrolysis of the irradiated product, ^{129}I formed by electron capture of ^{129}Xe appears entirely in the periodate form. A basic form of Xe(VI) was shown by paper electrophoresis.

64-68. Schumacher, Ernst, and Manfred Schaefer

PREPARATION AND QUALITATIVE PROPERTIES OF XENON TETRAFLUORIDE, *Helv. Chim. Acta* **47**(1), 150-4 (1964). (In German.)

XeF_4 was prepared by pumping a mixture of Xe and F_2 (1:3) at atmosphere pressure into a furnace at 560°C. In a connecting cooling apparatus at 0°C the crystallized XeF_4 was collected in a yield of 97%. XeF_4 (20 g) can be prepared in 2 hr. XeF_4 in a glass ampul affects the glass surface within 1 day at room temperature. XeF_4 smokes and gets warmer in open air, because of hydrolysis into Xe(OH)_4 . XeF_4 dissolves in H_2O , 100% AcOH , concentrated HNO_3 and H_2SO_4 . XeF_4 does not dissolve in CCl_4 , CS_2 , $\text{HCON(CH}_3)_2$, Et_2O , cyclohexane. It ignites with tetrahydrofuran, dioxane, ethanol, and cyclopentadiene. XeF_4 dissolves in water-free HF and can be regained unchanged therefrom.

64-69. Schwarz, H.

RARE GAS COMPOUNDS, *Naturwissenschaften* **51**, 397-403 (1964). (In German.)

Includes review of early attempts to prepare compounds, details of known compounds, and ideas on bonding.

64-70. Selig, Henry

XENON HEXAFLUORIDE COMPLEXES, *Science* **144**, 537 (1964).

XeF_4 reacts with BF_3 or AsF_5 at room temperature to form 1:1 adducts. The adducts are white solids with vapor pressures less than 1 mm at 20°C. The BF_3 complex can be sublimed under vacuum at 20°C, whereas the AsF_5 complex cannot be similarly sublimed. Both adducts are extremely hygroscopic and appear to react with Pyrex glass.

64-71. Selig, Henry, Howard H. Claassen, Cedric L. Chernick, John G. Malm, and John L. Huston

XENON TETROXIDE: PREPARATION AND SOME PROPERTIES, *Science* **143**, 1322-3 (1964).

Xenon tetroxide is a yellow solid at low temperature. It has a vapor pressure of about 25 mm-Hg at 0°C and

is unstable at room temperature. The infrared spectrum of the vapor shows it to have tetrahedral symmetry.

64-72. Selig, Henry, John G. Malm, and Howard H. Claassen

THE CHEMISTRY OF THE NOBLE GASES, *Sci. Am.* **210**, 66-77 (1964).

The history and chemistry of the rare gases and their compounds are discussed. Theoretical aspects of rare gas chemistry are also considered.

64-73. Selig, Henry, and Raymond D. Peacock

A KRYPTON DIFLUORIDE-ANTIMONY PENTAFLUORIDE COMPLEX, *J. Am. Chem. Soc.* **86**, 3895 (1964).

Preparation of the complex $KrF_2 \cdot 2SbF_5$ is reported. The compound is formed by treating KrF_2 with SbF_5 in glass or Kel-F. Reaction is complete at $-20^\circ C$, and if excess SbF_5 is present, most of the white crystalline material formed dissolves to give a clear yellowish solution at room temperature. The complex is more stable and much less volatile than the parent difluoride. It melts at about $50^\circ C$, but the liquid decomposes quickly to SbF_5 , Kr, and F. The infrared spectrum of the complex shows a strong characteristic absorption band at 813 cm^{-1} and other strong, poorly resolved absorptions in the $600\text{--}700\text{ cm}^{-1}$ region.

64-74. Serre, Josiane

FLUORIDES AND OTHER COMPOUNDS OF RARE GASES, *Bull. Soc. Chim. France*, 671-6 (1964). (In French.)

A review of experimental and theoretical work on noble gas compounds.

64-75. Sheft, Irving, Thomas M. Spittler, and Francis H. Martin

XENON HEXAFLUORIDE: PREPARATION OF PURE FORM AND MELTING POINT, *Science* **145**, 701-2 (1964).

Xenon hexafluoride forms an addition compound with sodium fluoride which can be used to separate it from the other xenon fluorides and oxyfluoride. The melting point of pure xenon hexafluoride prepared in this way was $47.7 \pm 0.2^\circ C$.

64-76. Shieh, Tsu-chia, N. C. Yang, and C. L. Chernick

REACTIONS OF OLEFINS WITH XENON FLUORIDES, *J. Am. Chem. Soc.* **86**, 5021-2 (1964).

Reactions of xenon fluorides with olefins are described. Products were identified by their infrared, nuclear magnetic resonance, and/or mass spectra. It was observed that XeF_6 is more reactive than XeF_4 while XeF_2 is less reactive.

64-77. Siegel, Stanley, and Elizabeth Gebert

CRYSTALLOGRAPHIC STUDIES OF KRYPTON DIFLUORIDE, *J. Am. Chem. Soc.* **86**, 3896 (1964).

Samples of KrF_2 were found to be sufficiently stable to enable crystallographic information to be obtained.

Single-crystal oscillation and Weissenberg patterns indicate that the symmetry is tetragonal, with $a = 6.533$ and $c = 5.831$ Å. The calculated X-ray density, assuming four molecules in the cell, is 3.24 g/cm^3 . The cell appears to be primitive and therefore is not isostructural with XeF_2 .

64-78. Slivnik, Joze

WORK ON THE SYNTHESIS OF XENON AND FLUORINE BINARY COMPOUNDS, *Nukl. Enerija* **1**, 15-16 (1964). (In Yugoslavian.)

The results of experiments on the separation of xenon tetrafluoride and xenon hexafluoride are described. The conditions of work are stated as well as some characteristics of the apparatuses. The chemical analysis and pressure measurements indicate the possibility of the existence of xenon octafluoride.

64-79. Starke, K., and E. Guenther

SZILARD-CHALMERS EFFECT IN SOLID XENON TETRAFLUORIDE, *Radiochim. Acta* **2**, 159-60 (1964).

A simple technique was used to detect at least qualitatively a possible Szilard-Chalmers effect in solid XeF_4 . Target samples weighing 9-50 mg were irradiated for 55 min with a neutron flux of $3 \times 10^{11}\text{ n/cm}^2$. For 37.2 mg of XeF_4 present before sublimation, a specific activity of 250 counts/min-mg was estimated. After two sublimations, 29.0 mg survived with a specific activity of about 140 counts/min-mg. It was concluded that the fraction of the activity present as elementary Xe is of the same order of magnitude as the retention. This would mean that in the solid a great number of recoil atoms pick up fluorine from neighboring XeF_4 molecules to form at least a difluoride.

64-80. Urch, D. S.

THE STEREOCHEMICALLY INERT LONE PAIR? A SPECULATION ON THE BONDING IN $SbCl_5$, $SeBr_4$, $TeBr_4$, IF_5 , XeF_6 , ETC., *J. Chem. Soc., Suppl. No. 1*, 5775 (1964).

Bonding in hexahalogen complexes of nontransition metals is discussed in terms of the relative involvement of s and d orbitals. For XeF_6 it is suggested that any distortions from O_h symmetry will be slight, and may well be offset by crystal forces in the solid.

64-81. Urch, D. S.

ELECTRONIC STRUCTURES OF KRYPTATES AND XENATES, *Nature* **203**, 403-4 (1964).

The electronic structures of kryptates and xenates are discussed. The models considered are based on regular octahedra and tetrahedra. This is reasonable only if the 4s (Kr) and 5s (Xe) orbitals are so tightly bound that they have no stereochemical effect. Since the formation of these anions depends on the s orbitals being tightly bound, this does not seem too extreme an assumption.

64-82. Vannerberg, Nils Gosta

CHEMISTRY OF THE NOBLE GASES, *Svensk Kem. Tidskr.* **76**, 693-9 (1964). (In Swedish.)

The formation and structure of noble gas compounds is described, and theories of bonding are discussed.

64-83. Wade, Charles G., and J. S. Waugh

SPIN LATTICE RELAXATION OF ^{19}F IN CRYSTALLINE XENON TETRAFLUORIDE, *J. Chem. Phys.* **40**, 2063-4 (1964).

The results of measurements of the spin-lattice relaxation time T_1 of the ^{19}F nuclei in crystalline XeF_4 at 30 Mc/sec over the temperature range from 77 to 373°K are presented. The plot is linear between 250°K and the melting point, indicating that the relaxation is dominated by a single type of thermally activated molecular motion. At low temperatures, however, the plot departs from linearity, and T_1 approaches a value of approximately 1000 sec at 77°K. The slope yields a value for the activation energy, E_a , of 12.0 ± 1.5 kcal/mole.

64-84. Zalkin, Allan, J. D. Forrester, and David H. Templeton

THE CRYSTAL STRUCTURE OF SODIUM PERXENATE HEXAHYDRATE, *Inorg. Chem.* **3**, 1417-21 (1964).

Crystals of $\text{Na}_4\text{XeO}_6 \cdot 6\text{H}_2\text{O}$ were studied by X-ray diffraction, and the subsequent crystal-structure analysis determined its composition. This material crystallizes in the orthorhombic space group $Pbca$, with $a = 18.44$, $b = 10.103$, and $c = 5.873$ Å. There are four molecules per unit cell, and the calculated X-ray density is 2.59 g/cc. The structure consists of two types of layers stacked alternately in the a direction and tied to each other by hydrogen bonds. One type of layer contains a hexagonal array of all of the perxenate and half of the sodium ions, and the second type has all of the water in octahedra about the remaining sodium ions. The perxenate ion in this salt is octahedral with an average Xe-O bond distance of 1.84 ± 0.02 Å.

64-85. Zalkin, Allan, J. D. Forrester, David H. Templeton, Stanley M. Williamson, and Charles W. Koch

POTASSIUM PERXENATE NONAHYDRATE, *J. Am. Chem. Soc.* **86**, 3569-71 (1964).

The preparation and properties of potassium perxenate nonahydrate are given. The crystal structure is shown and described by X-ray diffraction analysis.

64-86. Zimmermann, H. J., and G. G. Harvey

QUARTERLY PROGRESS REPORT NO. 72 [ON ELECTRONICS] TID-20256 (Jan. 15, 1964) 308p.

Research progress on radio physics, plasma dynamics, and communication sciences and engineering is summarized.

1965

65-1. Allen, Leland C.

THE FORMATION OF NOBLE GAS COMPOUNDS, *Ann. N. Y. Acad. Sci.* **118**, 883 (1965).

The development of the concept of the atomic closed shell is described. A summary is given of theoretical explanations used to describe chemical binding. An electron-correlation representation is shown to provide a useful qualitative and quantitative connection

between inert gas atoms and the existence of noble gas compounds.

65-2. Allen, Leland C., Robert M. Erdahl, and Jerry L. Whitten

HELIUM DIFLUORIDE, *J. Am. Chem. Soc.* **87**, 3769 (1965).

A many-electron valence-bond wave function for HeF_2 was constructed. For all geometries examined the molecular energy curve was repulsive. All twenty electrons were used in the calculation.

65-3. Appelman, E. H., and M. Anbar

INTERMEDIATES IN THE OXIDATION OF WATER BY PERXENATE, *Inorg. Chem.* **4**:1066-9 (July 1965).

The reactions that took place when solid sodium perxenate was dissolved in water and the solution subsequently acidified are written as follows: $\text{Na}_4\text{XeO}_6(\text{s}) + \text{H}_2\text{O} \rightarrow \text{HXeO}_4^- + \text{OH}^- + 4\text{Na}^+$ and $\text{HXeO}_4^- + 3\text{H}^+ \rightarrow \text{XeO}_3 + 1/2\text{O}_2 + 2\text{H}_2\text{O}$. The product was a stable solution of hexavalent xenon. The xenon(VI)-xenon(VIII) electrode potential was about 3 V, making a number of mechanisms possible for the second reaction. Among these were processes involving the direct transfer of one or more electrons to the xenon(VIII) from one of its ligand oxygens or from a solvent water molecule. Transfer of a single electron led to the formation of an OH radical and a transient xenon(VII) intermediate, whereas a double electron transfer from a single donor resulted in an oxygen atom in Xe(VI) . Studies indicated that the second reaction proceeds almost entirely through the formation of OH^\cdot radicals

65-4. Agron, Paul A., Carroll K. Johnson, and Henri A. Levy

XENON HEXAFLUORIDE: CRYSTALLOGRAPHIC DATA AND PHASE TRANSITIONS, *Inorg. Nucl. Chem. Lett.* **1**, 145-8 (1965).

The crystal structure of XeF_6 is being studied by X-ray and neutron diffraction. The structure of one modification of XeF_6 , crystallographic data on a second modification, and possible identification of the phase regions observed in the thermal study are reported. For the first modification, the following unit-cell dimensions were obtained: $a = 9.33$, $b = 10.96$, and $c = 8.95$ Å (standard errors, 0.03 Å), $\beta = 91.9 \pm 0.2^\circ$; probable space group $P2_1/m$ or $P2_1$. The theoretical density is 3.56 g cm^{-3} . Positions of the 8 Xe atoms in the unit cell were determined. The second modification was found to be fcc with $a = 25.34 \pm 0.05$ Å and a probable space group $F43c$ or $Fm3c$.

65-5. Bane, R. W.

THE SPECTROPHOTOMETRIC DETERMINATION OF MANGANESE AFTER OXIDATION WITH SODIUM PERXENATE, *Analyst* **90**, 756-8 (1965).

The use of sodium perxenate in the spectrophotometric determination of manganese is shown to eliminate the necessity of heating, maintaining at near-boiling temperature, and cooling to room temperature before spectrophotometric measurement. Some properties of sodium perxenate of interest in analytical chemistry are reviewed. The determination of manganese in uranium oxides and uranium alloys is described.

65-6. Bankowski, Zdzislaw, Andrzej Cybulski, and Jerzy Gromadowski

COMPOUNDS OF NOBLE GASES, *Wiadomosci Chem.* 19, 95-131 (1965). (In Polish.) English Translation: AEC Translation Series, AEC-tr-6609.

The chemical syntheses of noble gas compounds are reviewed, and the chemical and certain physical properties are outlined for KrF_2 , KrF_4 , XeF_2 , XeF_4 , XeF_6 , XeF_8 , for other more complex compounds of xenon, as well as for compounds of radon. The particulars of the structure, thermodynamics, and spectroscopy of the noble gas compounds are discussed, and the nature of the chemical bonding is considered theoretically. The possibilities of the existence of other noble gas compounds are discussed, and a few predicted compounds are mentioned. 88 References.

65-7. Bartell, L. S., R. M. Gavin, Jr., H. Bradford Thompson, and C. L. Chernick

MOLECULAR STRUCTURE OF XeF_6 , *J. Chem. Phys.* 43, 2547-8 (1965).

An electron-diffraction analysis was made of the structure of gaseous XeF_6 . Preliminary diffraction data ($11 \leq q \leq 124$) imply an average Xe-F bond length of $r_g = 1.90 \pm 0.01$ Å, which is consistent with the trend set by XeF_4 and XeF_2 . However, the molecule is appreciably distorted from O_h symmetry. The results confirmed the inference that gaseous XeF_6 is not a regular octahedron.

65-8. Begun, G. M., W. H. Fletcher, and D. F. Smith

VIBRATIONAL SPECTRA AND VALENCE FORCE CONSTANTS OF THE SQUARE-PYRAMIDAL MOLECULES— XeOF_4 , IF_5 , BrF_5 , and ClF_5 , *J. Chem. Phys.* 42, 2236 (1965).

The infrared and Raman spectra of XeOF_4 , IF_5 , BrF_5 , and ClF_5 were recorded. The data were tabulated, and assignments of the fundamental vibration and combination frequencies made on the basis of a square-pyramidal structure for these molecules. Valence force constants, based on estimated molecular parameters, were calculated for these molecules. Comparisons between the different members of the series showed that the bonding in XeOF_4 is remarkably similar to that in the interhalogen compounds.

65-9. Burns, John H., Raymond D. Ellison, and Henri A. Levy

THE CRYSTAL STRUCTURE OF THE MOLECULAR ADDITION COMPOUND XENON DIFLUORIDE-XENON TETRAFLUORIDE, *Acta Cryst.* 18, 11-16 (1965).

The crystal structure of the molecular addition compound xenon difluoride-xenon tetrafluoride was solved by a combination of heavy-atom and direct methods using three-dimensional X-ray-diffraction data. Structural parameters including anisotropic thermal motion were refined by the method of least squares. The existence in the crystal of discrete XeF_2 and XeF_4 molecules, with linear and square-planar configurations, respectively, was established, and a description of their thermal motions obtained. The short intermolecular distances in $\text{XeF}_2 \cdot \text{XeF}_4$ are similar to those in the crystals of the two components and suggest that there is electrostatic attraction between the molecules.

65-10. Claassen, Howard H., Gordon L. Goodman, John G. Malm, and Felix Schreiner

INFRARED AND RAMAN SPECTRA OF KRYPTON DIFLUORIDE, *J. Chem. Phys.* 42, 1229-32 (1965).

The infrared and Raman spectra of KrF_2 vapor were obtained. They clearly indicated a linear and symmetric molecule with the symmetric stretching frequency at 449 cm^{-1} , the asymmetric stretching frequency at 588 cm^{-1} , and the bending frequency at 232.6 cm^{-1} . The force constants are $f_r = 2.46$, $f_{rr} = -0.20$, and $f_a = 0.21 \text{ mdyn/Å}$. The negative bond-bond interaction constant can be explained neither by valence-bond models nor by a simple molecular-orbital model.

65-11. Claassen, Howard H., Henry Selig, and John G. Malm

XENON TETRAFLUORIDE AND PROCESS OF MAKING SAME, U.S. Patent 3,183,061 (May 11, 1965).

A process of preparing XeF_4 by reacting xenon and fluorine at 350 to 450°C and cooling is described. The properties of XeF_4 are discussed.

65-12. Cleveland, J. M.

OXIDATION OF PLUTONIUM(III) BY XENON TRIOXIDE, *J. Am. Chem. Soc.* 87, 1816 (April 20, 1965).

The reaction $6\text{Pu}^{3+} + \text{XeO}_3 + 6\text{H}^+ \rightarrow 6\text{Pu}^{4+} + \text{Xe} + 3\text{H}_2\text{O}$ was found to proceed at a measurable rate. The oxidation reaction was studied at $30.0 \pm 0.2^\circ\text{C}$ in perchlorate solutions. Data indicated that the reaction is second order and described by the rate expression $-d[\text{Pu}^{3+}]/dt = k[\text{Pu}^{3+}][\text{XeO}_3]$, with k having an average value of $1.6 \times 10^{-2} \text{ l/mole-sec}$ at 30°C .

65-13. Contamin, Ghislaine

LES COMPOSES DES GAS RARES (NOBLE GAS COMPOUNDS), CEA-Bib-61, 50p (1965).

Preparations and properties of noble gas fluorides, their oxygenated compounds, and other derivatives are described. The various theories which have been put forth up to now in order to explain the structure of these compounds are briefly reviewed.

65-14. Dwyer, O. E., and R. H. Wiswall

CHEMISTRY AND CHEMICAL ENGINEERING DIVISION, BNL-900 (pp. 29-72) 1965.

A progress report covering work on many problems. ... The fluorocarbon analogs of biphenyl, naphthalene, o-terphenyl, and bicyclohexyl were exposed to $\approx 8 \times 10^7$ rads of gamma radiation. The most stable compound was F-biphenyl, which was markedly superior at 500°C to aromatic hydrocarbons. Exposure of Kr-F_2 mixtures, held at -140°C , to a beam of protons from the cyclotron resulted in the formation of KrF_2 in good yield. ...

65-15. Fung, Bing-Man

THE ELECTRONEGATIVITY OF NOBLE GASES, *J. Phys. Chem.* 69, 596-600 (1965).

Three methods are discussed for the calculation of electronegativities based on (i) bond energies, (ii) covalent radii, and (iii) ionization potentials and

electron affinities. The selected values are:

| He | Ne | Ar | Kr | Xe | Rn |
|---------|-----|-----|-----|-----|---------|
| 2.5-3.0 | 4.4 | 3.5 | 3.0 | 2.6 | 2.3-2.5 |

Based on electronegativity considerations one might expect the existence of HNe^+ , CF_3Ne^+ , and BF_3Ne .

65-16. Groz, Peter, Istvan Kiss, Andras Revesz, and Tamas Sipos

PRODUCTION OF XeF_2 , Magyar Tud. Akad. Kozp. Fiz. Kut. Int. Kozlemen. 13, 283-90 (1965). (In Hungarian.)

XeF_2 was produced by circulating a mixture of Xe and F_2 through a Monel tube reactor filled with nickel plates kept at 500°C and trapping out the product before passing back to the reaction zone. The compound was analyzed by chemical methods and mass spectrometry. It has a melting point at $130 \pm 0.6^\circ\text{C}$ and by optical measurements was found to crystallize in the monoclinic system. Some qualitative reactions observed on the XeF_2 are described.

65-17. Gunn, Stuart R.

THE HEAT OF FORMATION OF XENON TETROXIDE, J. Am. Chem. Soc. 87, 2290-1 (1965).

The heat of explosive decomposition of the XeO_4 gas to its constituent elements at 25°C was measured. The oxygen and xenon obtained were analyzed mass spectrometrically. The heat of formation of $\text{XeO}_4(\text{g})$ was calculated to be 153.5 kcal/mole. Results indicated that XeO_3 was either not formed in the decomposition or that any produced was subsequently decomposed to the elements. The thermochemical bond energy of XeO_4 was calculated to be 21.1 kcal. Heats of formation of xenon oxyfluorides were estimated from these values.

65-18. Haissinsky, M., and J. -P. Adloff

RADIOCHEMICAL SURVEY OF THE ELEMENTS, Principal Characteristics and Applications of the Elements and Their Isotopes, Translation by Express Translation Service of Dictionnaire Radiochimique des Elements, New York [American] Elsevier Publishing Company, 1965. 185p

The radiochemical properties of the elements are discussed. Nuclear, chemical, and physical properties are described for each of the elements and their isotopes.

65-19. Holcomb, H. Perry

ANALYTICAL OXIDATION OF AMERICIUM AND SODIUM PERXENATE, Anal. Chem. 37, 415 (1965).

The oxidation of Am(III) to Am(VI) in acid solution was studied, using solid Na_4XeO_6 as oxidant. In the presence of Ag(I) the oxidation goes to 95% completion, but only to 91% without the Ag(I) . Because of the high oxidation potential of the $\text{Am(VI)}-\text{Am(III)}$ couple, tracer quantities of americium are difficult to keep oxidized. Sodium perxenate, being a powerful oxidant, probably oxidizes the americium and silver almost instantaneously, and itself decomposes. The Ag(II) then serves as a holding oxidant for Am(VI) .

65-20. Hoppe, R.

CHEMISTRY OF THE RARE GASES, Fortschr. Chem. Forsch. 5, 213-346 (1965). (In German.)

A thorough review of the chemical and physical properties of the noble gas compounds, complete to mid-1965. 341 References.

65-21. Kamemoto, Yuichiro

FORMATION OF FISSION-XENON COMPOUNDS, Nippon Kagaku Zasshi 86, 648-9 (1965). (In Japanese.) Translated in J. Inorg. Nucl. Chem. 27, 2678-9, 1965.

Fission-xenon compounds were prepared by neutron irradiation of mixture of uranium dioxide powder and lithium fluoride powder. The mixture was irradiated in the JRR-1 reactor for 1 day at a neutron flux of about 3×10^{11} n/cm²/sec and cooled for 20 days. Then the mixture was placed at the bottom of a glass tube and heated at 450°C . The evaporated substances were deposited on the lower-temperature portion of the glass wall. After cooling this tube, the glass wall was surveyed by a γ spectrometer. The activity due to ^{133}Xe was observed on it. After elementary xenon in the tube was removed by evacuating or blowing air, the tube was surveyed again. The presence of xenon activity after the elementary xenon had been removed, revealed the formation of xenon compounds.

65-22. Kamemoto, Y.

PREPARATION OF XENON COMPOUND BY ACTIVATION PROCESSES FOR FLUORIDE SYSTEM, J. Inorg. Nucl. Chem. 27, 2678-9 (1965).

Xenon compounds were prepared by using nuclear fission recoil. A lithium fluoride and uranium dioxide powder mixture in a weight ratio of 4:1 was irradiated at a neutron flux of about 3×10^{11} n/cm²/sec for 1 day. The irradiated mixture was sealed in an evacuated glass tube and then heated at 450°C for 5 hr. The count rates from ^{133}Xe obtained at different position on the glass tube are shown. The results showed that the xenon compounds formed were not produced by the action of the decay energy of iodine, but were produced by some action of either the nuclear recoil energy, in-pile gamma rays, or heat of the alpha particles of lithium, or of a combination of them all.

65-23. Kirin, I. S., Yu. K. Gusev, A. N. Mosevich, N. P. Kusnetsov, and V. S. Gusel'nikov

SEPARATIONS OF XENON TRIOXIDE AND IODIC ACID ON ZIRCONIUM PHOSPHATE, Radiokhimiya 7, 736-8 (1965). (In Russian.) English Translation: Radiochemistry (USSR) 7, 737-9 (1965).

Zirconium phosphate was used for the chromatographic separation of XeO_3 from HIO_3 , the XeO_3 having been prepared by β -disintegration of I-131 contained in HIO_3 . The column was 3 mm in diameter and 50 mm long. The use of 0.4 M KNO_3 as eluent resulted in the IO_3^- being retained on the column; it could be quantitatively removed with a 1 M solution of K_2SO_4 at pH = 10.5.

65-24. Koch, Charles W., and Stanley M. Williamson
A STUDY ON THE STABILITY OF XENON TRIOXIDE
IN BASIC SOLUTIONS, pp. 182-3 in UCRL-11828, 1965.

A study was made of the stoichiometry of the reaction between XeO_3 and KOH in solution. The results show that the reaction is more complex than the simple disproportionation of XeO_3 followed by decomposition of Xe(IV) . A 25 to 33% yield of perxenate is obtained for 0.3 to 3 M KOH, and the evolved O_2/Xe ratio is greater than unity. As the decomposition progresses, a yellow, insoluble, explosive compound is formed. In one experiment, when the solution was reduced by vacuum distillation, $\text{K}_4\text{XeO}_6 \cdot 9\text{H}_2\text{O}$ was formed.

65-25. Krishnamachari, S. L. N. G.,
N. A. Narasimham, and Mahavir Singh

ULTRAVIOLET EMISSION SPECTRA OF XENON
AND KRYPTON FLUORIDES, Current Sci. (India) 34,
75-7 (1965).

During investigations of the emission spectra obtained in discharges through BF_3 in the presence of xenon and krypton, spectral features were observed in the region from 2200 to 3500 Å, which were attributable to fluorides of xenon and krypton. Characteristics of the spectra are described.

65-26. Maiti, Sukumar

THE CHEMISTRY OF THE NOBLE GASES, Sci. Cult.
(Calcutta) 31, 108-19 (1965).

The history of the discovery of the rare gases and early attempts to prepare chemical compounds of them are discussed. Preparation of XePtF_6 and other fluorides of xenon is described. Preparation of xenon oxygen compounds, complex xenon compounds, krypton fluorides, radon fluorides, and helium fluorides is discussed. The nature of bonding in the rare gas compounds is considered, and the octahedral hybrid model, correlation-effects model, molecular orbital model, and valence-bond resonance model are described.

65-27. Maly, Jacques

CHEMICAL COMPOUNDS OF THE RARE GASES AND
THE REACTIVITY OF FLUORINE, Ann. Chim. (Paris)
10, 455-66 (1965). (In French.)

The preparation and chemistry of compounds of the rare gases is discussed, including preparation of the first compounds of xenon, preparation and properties of F compounds (table), preparation and chemistry of O compounds (oxyfluorides, oxides, xenates, and perxenates, to include reactions in acid and alkaline solution), and preparation of complexes. Structures of principal compounds are reviewed on the basis of IR and crystallographic data (table), with sections on structures of F compounds, and structures of oxides and perxenates. Experimental studies of the nature of the bonds are outlined, including thermochemical studies in relation to other fluorides, and studies of the partial ionic character of the bonds by F nuclear magnetic resonance and by Mössbauer-effect studies using ^{129}Xe . A short discussion of the particular chemical properties of F (dissociation energy, bond strength in halogens and hydrohalic acids, ionization potential, and electron affinity) is given. Theoretical studies of bond formation in rare gases are then reviewed.

65-28. Malm, John G., Felix Schreiner, and
Darrell Osborne

THE PREPARATION AND SOME THERMAL PROPERTIES
OF PURE XENON HEXAFLUORIDE, Inorg.
Nucl. Chem. Letters 1, 97-100 (1965).

A pure sample of XeF_6 was prepared by reacting xenon and fluorine at 250°C for 150 hr in the presence of finely divided sodium fluoride. The XeF_6 forms a complex with NaF under the preparative conditions, while the possible impurities (XeF_2 , XeF_4 and XeOF_4) do not. The impurities are removed by pumping at temperatures up to 50°C. Finally, the complex is dissociated at 150°C, yielding pure XeF_6 .

65-29. Malm, John G., Henry Selig, Joshua Jortner,
and Stuart A. Rice

THE CHEMISTRY OF XENON, Chem. Rev. 65, 199-236
(1965).

All experimental and theoretical works on the chemistry of xenon published through June 1964 are reviewed. The study of xenon chemistry is limited to the stable fluorides and their complexes, two unstable oxides, and the aqueous species derived from the hydrolysis of the fluorides. The nature of the chemical bond in xenon fluorides is discussed. Interpretations of physical properties are considered, along with excited electronic states. Theoretical models are discussed.

65-30. Malm, John G., Irving Sheft,
Cedric L. Chernick, and Harold H. Claassen

XENON HEXAFLUORIDE AND METHOD OF MAKING,
U.S. Patent 3,192,016 (June 29, 1965).

A process for preparing xenon hexafluoride that comprises heating xenon gas and at least 10 moles of fluorine gas per mole of xenon in a closed system to between 200 and 400°C is described.

65-31. Melton, Charles E., and Hubert W. Joy

CALCULATED IONIZATION POTENTIAL OF
CHLORO- AND FLUOROMETHANES, TETRA-
FLUOROMETHANE (CF_4), XENON TETRAFLUORIDE
(XeF_4), AND XENON TETRACHLORIDE (XeCl_4),
J. Chem. Phys. 42, 2982-3 (April 15, 1965).

An energy-calibrated molecular-orbital method in the LCAO approximation was used to calculate the ionization potentials for methane, chloro- and fluoromethanes, xenon tetrafluoride, and xenon tetrachloride.

65-32. Miller, Glenn H., and J. R. Dacey

THE IMPORTANCE OF XENON FLUORIDES IN THE
XENON-PHOTOSENSITIZED REACTION OF THE
PERFLUOROALKANES, J. Phys. Chem. 69, 1434-5
(1965).

The role of xenon fluorides in the xenon-photosensitized reactions of perfluoroalkanes is discussed. The reactions of $\text{C}_2\text{-C}_4\text{F}_8$ are used as an example. It was concluded that the main initial step is $\text{Xe}^* + \text{C}_2\text{-C}_4\text{F}_8 \rightarrow \text{XeF}_2 + \text{C}_2\text{-C}_4\text{F}_6^*$.

65-33. Moody, G. J., and J. D. R. Thomas

β -DECAY IN PREPARATIVE NOBLE GAS CHEMISTRY, *Nature* **206**, 613 (1965).

The general principle that the abundance of an intact parent carbon-noble gas ion depends on the carbon-noble gas bond strength, as well as the recoil energy imparted to such bonds from β decay is discussed. The possibility of preparing a neon fluoride as well as chlorides and bromides of xenon are considered.

65-34. Morrow, Scott I., and Archie R. Young, II

THE REACTION OF XENON WITH DIOXYGEN DIFLUORIDE. A NEW METHOD FOR THE SYNTHESIS OF XENON DIFLUORIDE, *Inorg. Chem.* **4**, 759-60 (1965).

The reactions of dioxygen difluoride with xenon and krypton at low temperatures were analyzed. No reaction was observed with krypton up to -78°C , at which O_2F_2 rapidly decomposed. Xenon, on the other hand, was converted quantitatively to a yellow solid by reaction with a large excess of O_2F_2 at -118°C . When this solid was sublimed at 50°C , high yields of xenon difluoride were obtained.

65-35. Mosevich, A. N., N. P. Kuzenetsov, and Yu. K. Gusev

CHROMATOGRAPHIC SEPARATION OF CERTAIN XENON AND IODINE OXYGEN COMPOUNDS, *Radiokhimiya* **7**, 678-87 (1965). English Translation: *Radiochemistry (USSR)* **7**, 677-84 (1965).

By means of radioactive tracers, the behavior of XeO_3 and the anions 10_3^- and 10_4^- on the ionites aluminum oxide, zirconium hydroxide, zirconium phosphate, and Amberlite IRA-400 was investigated, and the conditions for separating XeO_3 from solutions containing iodate and periodate were determined. It was found that when gaseous xenon is present in the solutions, it is eluted from the XeO_3 on cleared columns of aluminum oxide, zirconium hydroxide, and Amberlite IRA-400. The chromatographic separation of the mixture XeO_3 - 10_3^- - 10_4^- on zirconium hydroxide, zirconium phosphate, and Amberlite IRA-400 was carried out. Chemically bound xenon-131 m, formed as a result of the β decay of ^{131}I in the compound HIO_3 , was separated in pure form by the addition of XeO_3 as carrier.

65-36. Murin, A. N., I. S. Kirin, V. D. Nefedov, S. A. Grachev, and Yu. K. Gusev

CHEMICAL CHANGES IN THE β -DECAY OF IODINE ISOTOPES AS A METHOD OF SYNTHESIZING XENON COMPOUNDS, *Dokl. Akad. Nauk SSSR* **161**, 611-13 (1965). (In Russian.) English Translation: *Proc. Acad. Sci. USSR, Chem.* **161**, 312-14 (1965).

The formation of oxygen compounds of xenon on decay of the corresponding ^{131}I compound was demonstrated. In a solution of $\text{K}^{131}\text{IO}_4$ in dilute sulfuric acid, approximately 40% of the daughter ^{131}Xe that was formed accumulated in chemically combined form. With K^{131}I combined xenon was not found. In these experiments the iodine compounds were dissolved in water or $0.02 \text{ N H}_2\text{SO}_4$ and the free xenon was removed by a current of helium. Then a reductant was added and helium was again passed through to remove free xenon. The theory is that in the conversion of ^{131}I as

iodate or periodate ion, in the first instant of radioactive decay neutral molecules of XeO_3 or XeO_4 are formed. Approximately half these molecules are in the activated state. Cessation of the activation may be accompanied by release of oxygen and formation of a lower oxidation state, even free xenon. Octavalent xenon is very unstable in acid solution.

65-37. Murin, A. N., V. D. Nefedov, I. S. Kirin, S. A. Grachev, Yu. K. Gusev, and G. N. Shapkin

USE OF β DECAY OF BROMINE ISOTOPES AS A POSSIBLE METHOD FOR SYNTHESIS OF KRYPTON COMPOUNDS, *Zh. Obshch. Khim.* **35**, 2137-40 (1965). (In Russian.) English Translation: *J. Gen. Chem. (USSR)* **1965** **35**, 2126.

The possibility of using the chemical changes occurring during the β decay of bromine isotopes for synthesis of the fluorides and oxides of krypton is suggested. A method for the analysis of krypton compounds is proposed.

65-38. Murin, A. N., V. D. Nefedov, I. S. Kirin, V. V. Leonov, V. M. Zaitsev, and G. P. Akulov

FORMATION OF FLUORINE-CONTAINING COMPOUNDS OF XENON DURING β DECAY OF ^{131}I CONTAINED IN IODINE PENTAFLUORIDE, *Radiokhimiya* **7**, 629-30 (1965). (In Russian.)

Free ^{131}Xe was accumulated by bubbling helium for 8 hr at room temperature through liquid $^{131}\text{IF}_5$. The origin of this free ^{131}Xe was traced to the intermediate formation of a molecular ion $[^{131}\text{XeF}_5]^+$. After removal of free ^{131}Xe , the β -decaying material was hydrolyzed and the products of hydrolysis were subjected to reduction with various reducing agents. In the course of treatment with HCl the xenon fluorine compounds were reduced to free xenon. No free xenon was obtained when KI , hydroxylamine, or Fe^{2+} was used as a reducing agent. It was found that the xenon fluorine compounds are more volatile than the starting $^{131}\text{IF}_5$.

65-39. Murin, A. N., V. D. Nefedov, I. S. Kirin, S. A. Grachev, Yu. K. Gusev, and Yu. P. Saikov

FORMATION OF OXYGEN-XENON COMPOUNDS DURING β -RADIATION OF ^{133}I INCORPORATED IN POTASSIUM PERIODATE, *Radiokhimiya* **7**, 631-2 (1965). (In Russian.) English Translation: *Radiochemistry (USSR)* **7**, 629-30 (1965).

Xenon oxides (XeO_4 and XeO_3) were prepared by β decay of ^{131}I in KIO_4 . Helium gas was bubbled for 30 min at a rate of 26 ml/min through a solution of $\text{K}^{131}\text{IO}_4$ and K^{131}I in $0.002 \text{ N H}_2\text{SO}_4$ to remove free xenon. The elemental iodine was removed from the gas stream by passing helium through a KOH absorber. The xenon oxides were trapped on AG-5 activated carbon at liquid nitrogen temperature. The quantity of trapped ^{131}Xe was measured using an AI-100-1 analyzer. It was found that XeO_4 is unstable in acidic media and decomposes to XeO_3 .

65-40

ISOTOPE CHEMISTRY, ORNL-3832, pp. 33-49, 1965.

A progress report covering work on many problems. ... The infrared and Raman spectra of IOF_3 were recorded, and spectral assignments were made on the

basis of an octahedral structure with a fourfold symmetry axis. Valence force constants were calculated. Methods used for the vibrational analysis of molecules were compared. Force constants were calculated from spectral data for the molecules XeF_2 , XeF_4 , XeOF_4 , NH_3 , and BF_3 , ...

65-41. Perlow, G. J., and M. R. Perlow

PRODUCTION OF XENON COMPOUNDS BY THE BETA DECAY OF IODINE IN IODINE COMPOUNDS, Chemical Effects of Nuclear Transformations 2, 443-458 (1965). Proc. IAEA Symp. (See 64-64.)

Beta decay ^{129}I - ^{129}Xe in an iodine compound was studied by use of the Mössbauer effect in ^{129}Xe . In the first experiments a source of Na^{129}I was used with absorbers of hydroquinone clathrate, Na_4XeO_6 , XeF_4 , and XeF_2 . Single-line spectra were observed for the clathrate and perxenate, and two-line spectra for the fluorides. The single line indicates that in the source $\text{I}^- \rightarrow \text{Xe}^0$, its iso-electronic daughter. When $\text{Na}_3\text{H}_2\text{IO}_6$ was used as source, with clathrate absorber, the recoilless fraction increased by a factor of 3, implying stronger bonding. KIO_4 also gave a single but somewhat less intense line. With NaIO_3 as source and clathrate absorber, splitting was observed suggesting that $\text{IO}_3^- \rightarrow \text{XeO}_3$. This was verified by the observation of identical splitting in an XeO_3 absorber used with KIO_4 source. An experiment with $\text{KICl}_4 \cdot \text{H}_2\text{O}$ as source and clathrate absorber showed splitting somewhat smaller than in XeF_4 . Here $\text{ICl}_4^- \rightarrow \text{XeCl}_4$. By use of aligned crystals of $\text{KICl}_4 \cdot \text{H}_2\text{O}$ and making quantitative intensity measurements, it was established that the square planar structure of ICl_4^- is preserved in the transition of XeCl_4 and that XeCl_2 and Xe^0 are not formed in the reaction in detectable amounts. With $\text{Na}_3\text{H}_2^{131}\text{IO}_6$ as source the effect was observed in ^{131}Xe . Comparing XeF_4 spectra in both isotopes calibrated the splitting in ^{129}Xe and enabled quantitative comparison of XeF_4 and XeCl_4 with ICl_4^- , and of XeO_3 with IO_3^- . The unsplit KIO_4 spectrum implies that the tetrahedral ligand environment of the iodine is preserved in the resulting XeO_4 . Similarly, the paraperiodate result is consistent with preservation of its octahedral environment.

65-42. Schreiner, F., J. G. Malm, and J. C. Hindman

THE PREPARATION AND NUCLEAR MAGNETIC RESONANCE OF KRYPTON DIFLUORIDE, J. Am. Chem. Soc. 87, 25-8 (1965).

Krypton difluoride was prepared by passing an electric discharge through a mixture of the elements at low pressure (~20 mm) and low temperature (-183°C). This method was reported previously to yield krypton tetrafluoride, a claim which could not be substantiated by the present work. The compound obtained was a white crystalline solid which sublimed at temperatures well below 0°C and could be handled in dry, Pyrex glass or polychlorotrifluoroethylene containers. It was a highly reactive fluorinating agent which could be kept at dry ice temperature. At room temperature spontaneous decomposition occurred. Analytical data are given which establish the formula KrF_2 . Also, nmr measurements of the chemical shift for fluorine-19 of KrF_2 dissolved in anhydrous hydrofluoric acid are reported. The shielding value σ_{F_2} was found to be 374×10^{-6} for a solution of 4.6 moles of KrF_2/kg of HF

and 362×10^{-6} for a solution of 16.4 moles of KrF_2/kg of HF, both measured at 0°. These values agree with the value reported for a sample of krypton tetrafluoride (373×10^{-6}) which provides evidence that, in fact, the measurements were performed on krypton difluoride. Theoretical considerations treating the bonding in KrF_2 as analogous to that in XeF_2 lead to a shielding value which is in excellent agreement with the experimental one.

65-43. Selig, H., C. L. Chernick, C. W. Williams

THE REFRACTIVE INDEX AND MOLAR REFRACTION OF XENON OXIDE TETRAFLUORIDE, Inorg. Nucl. Chem. Lett. 1, 17-20 (1965).

The refractive index and density of XeOF_4 were measured. The XeOF_4 was prepared by partial hydrolysis of XeF_6 . The refractive index of two samples was 1.4279 at 4861 Å, 1.424 at 546 Å, and 1.4215 at 5893 Å. The density at 30.50°C was 3.071 g/cm³, and the measurements obeyed the equation $d = 3.168 - 0.0032t$.

65-44. Shamir, Jacob, H. Selig, David Samuel, and J. Reuben

THE PREPARATION AND OXYGEN-17 NUCLEAR MAGNETIC RESONANCE SPECTRUM OF $\text{XeO}^{17}\text{F}_4$, J. Am. Chem. Soc. 87, 2359-60 (1965).

The preparation and ^{17}O NMR spectrum of $\text{Xe}^{17}\text{OF}_4$ is described. The ^{17}O chemical shift is -313 ± 2 ppm (relative to H_2^{17}O), and the ^{129}Xe - ^{17}O spin-spin coupling constant is 692 ± 10 cps.

65-45. Spittler, T. M., and Bruno Jaselski

PREPARATION AND PROPERTIES OF MONOALKALI XENATES, J. Am. Chem. Soc. 87, 3357-60 (1965).

Monosodium, -potassium, -cesium, and -rubidium xenates were prepared by lyophilization of 0.1 M xenon trioxide and alkali hydroxides in 1:1 ratio. The existence of alkali xenates was confirmed by infrared spectroscopy, X-ray powder diffraction patterns, and determination of the oxidation equivalent by the "hi-lo" titration method. Sodium xenate had an apparent formula weight of 247 ± 4 . Sodium xenate is more stable than xenon trioxide and less stable than sodium perxenate. At room temperature, sodium xenate does not react readily with anhydrous methyl alcohol. The salt of sodium xenate is stable under anhydrous conditions, otherwise it disproportionates to xenon(0) and xenon(VIII).

65-46. Streng, L. V., and A. G. Streng

FORMATION OF XENON DIFLUORIDE FROM XENON AND OXYGEN DIFLUORIDE OR FLUORINE IN PYREX GLASS AT ROOM TEMPERATURE, Inorg. Chem. 4, 1370-1 (1965).

Formation of XeF_2 from xenon and oxygen difluoride or fluorine was found to occur in a Pyrex glass flask at room temperature and atmospheric pressure when exposed to ordinary daylight. The XeF_2 crystals grew to a size of 3 to 5 mm. The initial rate of formation was about 35 mg/day. The total amount of product obtained in 3 weeks varied from 0.5 to 0.75 g. There was no reaction in darkness.

65-47. Svec, Harry J.

MASS SPECTROMETRY OF VOLATILE INORGANIC COMPOUNDS, USAEC Report IS-983, Nov. 1, 1965. 31p. (CONF-640812-1). From Meeting on Mass Spectrometry, Glasgow, Aug. 24-Sept. 10, 1964.

Results of mass spectra of volatile inorganic halides, metal carbonyls, and hydrides are reported, and problems associated with the measurements are discussed. It was concluded that the application of appearance-potential data to calculating thermochemical properties of inorganic compounds not amenable to calorimetric measurements can be on firm ground if enough is known about all of the parameters involved in an appearance potential value.

65-48. Thomson, Bruce

CHEMISTRY OF THE NOBLE GASES, *Advance Sci.* **22**, 208-17 (1965).

Recent developments in the chemistry of He, Ne, Ar, Kr, Xe, and Rn are reviewed, particularly in the formation of compounds by these rare gases. The first true compound of a noble gas, xenon hexafluoroplatinate, $\text{Xe}^+(\text{PtF}_6)^-$, was prepared in 1962. Later, it was found that xenon combined with other metal hexafluorides at room temperature according to the equation: $\text{Xe} + \text{MF}_6 = \text{Xe}^+(\text{MF}_6)^-$, where $\text{M} = \text{Pt}, \text{Pu}, \text{Ru}, \text{Rh}$. XeF_2 was first noticed mass spectrometrically as an impurity in XeF_4 samples, but was soon produced quantitatively by UV photolysis of Xe and F_2 . Fluorides of the other noble gases were formed soon after the isolation of XeF_2 and XeF_4 , but the most stable rare gas fluoride to date is XeF_4 . Attempts to prepare the oxides by synthesis from the elements proved impossible. XeO_3 was first obtained as the dangerously explosive, nonvolatile, hydrolysis product of XeF_4 . Reactions of some of the xenon compounds are considered.

65-49. Trofimov, A. M., and Yu. N. Kazankin

CLATHRATE COMPOUNDS OF p-CRESOL WITH RARE GASES. PART I. COMPOUND OF p-CRESOL WITH XENON, *Radiokhimiya* **7**: 288-92 (1965). (In Russian.)

Xenon was reacted with p-cresol, and the formula of the clathrate formed was calculated by analyzing curves of the vapor pressure over the solid phase and over the region where both the solid and the liquid phases are present. The compound was assigned the formula $\text{Xe} \cdot 6\text{C}_7\text{H}_8\text{O}$. A gravimetric analysis of the compound confirmed this formula. The dissociation pressure of the compound at 25 to 35°C was determined, and from these data, the heat of formation of $\text{Xe} \cdot 6\text{C}_7\text{H}_8\text{O}$ from solid and liquid p-cresol was calculated to be 6100 and 23,000 cal/mole, respectively. The apparatus used in the synthesis and in the measurements of the vapor pressure is described.

65-50. Yeranós, Walter A.

NORMAL COORDINATE ANALYSIS OF XeF_4 IN THE UREY-BRADLEY FIELD, *Mol. Phys.* **9**, 449-54 (1965).

By means of published infrared and Raman data, the normal coordinates, the Urey-Bradley force constants,

and the contribution of these force constants to the different normal modes of XeF_4 were determined. The analysis was carried out using a Fortran II program written specifically for the IBM 1620 computer, and within the formalism of Wilson's G-F matrix method. Furthermore, using a recently reported semi-empirical MO scheme for XeF_4 , the vibronic interactions responsible for the symmetry-forbidden $2a_{1u} \rightarrow 3e_u$ electronic transition at 44.15 kK are discussed qualitatively.

65-51. Yeranós, W. A.

NORMAL COORDINATE ANALYSIS OF XeOF_4 IN THE UREY-BRADLEY FIELD, *Bull. Soc. Chim. Belges* **74**, 407-13 (1965).

By means of published infrared and Raman data, the Urey-Bradley force constants of XeOF_4 were determined. The analysis was carried out within Wilson's G-F matrix method and the constants evaluated by the use of a computer program, which refined the differences of the experimental and calculated frequencies in the least-squares sense. The G and F matrix elements, in both the GVFF and UBFF, of any molecule of the type MYX_4 and of C_{4v} symmetry are reported ($\alpha = \gamma = 90^\circ$). The normal coordinates, as well as the potential-energy-distribution matrix, of XeOF_4 in the field force determined are given.

65-52. Yeranós, W. A.

VIBRATIONAL ANALYSIS OF IO_4^- AND XeO_4 , *Bull. Soc. Chim. Belges* **74**, 414-17 (1965).

The vibrational spectrum and the potential constants of IO_4^- and XeO_4 were studied. The following data are presented: observed and calculated frequencies; Urey-Bradley force constants; normal coordinates; the potential-energy distribution.

1966

66-1. Adloff, J. P.

NOBLE GAS COMPOUNDS IN RADIOCHEMISTRY, *Radiochim. Acta* **6**, 1-9 (Aug 1966). (In French.)

Radiochemistry has to deal in its various fields with the noble gas compounds. The following aspects are considered: radon chemistry, radioinduced and radio-synthesis of these compounds, Szilard-Chalmers effect, and application of Mössbauer spectrometry to the investigation of the chemical state of nascent rare gas atoms. Possible formation of radon compounds as a result of the disintegration of radium is also discussed.

66-2. Allen, Leland C., Arthur M. Lesk, and Robert M. Erdahl

THE FLUORIDES AND OXIDES OF HELIUM AND NEON, *J. Amer. Chem. Soc.* **88**, 615-16 (1966).

High-accuracy, many-electron, valence-bond wave functions were obtained for HeF , HeO , NeF , NeF_2 , and NeO . The potential-energy curves for all species were repulsive. The valence-bond wave functions were constructed using the exact Hamiltonian with simultaneous inclusion of all the electrons. The NeO wave function includes the chemical structures NeO , Ne^+O^- ,

and $\text{Ne}^{2+}\text{O}^{2+}$, and is composed of 16 states made up from twenty-four 18×18 determinants. The chemically significant terms in the wave functions for the various species are given. Among the singly ionized states there are three in NeO and one in HeO that significantly lower the energy through formation of electron-pair bonds between open shells on each atom. Hybridization in the ionic states is discussed for these compounds.

66-3. Asimov, Isaac

NOBLE GASES, New York, Basic Books, Inc., 1966. 178p. \$4.50.

A study of the noble gases is presented that includes the history of the six gases, their composition and sources, events that led to the knowledge that noble gases could form compounds, and description of their application in modern science and industry.

66-4. Bankowski, Z.

COVALENT RADII OF NOBLE GAS ATOMS AND POSITION OF HYDROGEN IN THE PERIODIC SYSTEM OF ELEMENTS, *Nature* **209**, 71 (1966).

The electronegativities of the noble gases were calculated from ionization potentials and electron affinities, and the degrees of ionicity in known Xe-F and Xe-O bonds have been computed from the electronegativities. Electronegativity differences were used to calculate average covalent radii of Xe (single bond) = 1.41 \AA and Xe (double bond) = 1.18 \AA . The results show the covalent radius to be about 6% larger than that of the preceding element (iodine). Covalent radii for the other noble gases are estimated at 6% larger than their respective, preceding halogens:

| | | | | |
|----------------------|----------------------|-------------------|-------------------|-------------------|
| Ne | Ar | Kr | Xe | Rn |
| (0.76 \AA) | (1.05 \AA) | 1.21 \AA | 1.41 \AA | 1.55 \AA |

66-5. Bartell, L. S.

GILLESPIE'S MODEL, MOLECULAR ORBITALS, AND MOLECULAR STRUCTURE, *Inorg. Chem.* **5**, 1635-36 (1966).

The Gillespie model successfully correlates a great deal of stereochemical behavior with few empirical rules. But, the simple MO theory is equally valid if s orbitals are included.

The simple Hückel model (which altogether "neglects" explicit electron repulsions) closely parallels the Gillespie model (which considers "only" electron repulsions). This parallelism includes not only molecular geometries but also distributions of electron pairs. Localized MO's constructed from the delocalized MO's exhibit very Gillespie-like shifts in centers of gravity.

66-6. Bartlett, Neil, Fred Einstein, D. F. Stewart, and James Trotter

THE PREPARATION, CRYSTAL STRUCTURE, AND MAGNETIC PROPERTIES OF PENTAFLUORO-XENONYL HEXAFLUOROPENTATE(V), $[\text{XeF}_5]^+ [\text{PtF}_6]^-$, *Chem. Commun.*, No. 15, 550-2 (Aug. 10, 1966).

Studies were made of the crystal structure and magnetic properties of F_{11}PtXe formed during reactions between xenon, fluorine, and PtF_5 . A single-crystal X-ray structure determination of F_{11}PtXe disclosed a

molecular geometry consistent with an ionic formulation $(\text{XeF}_5)^+(\text{PtF}_6)^-$. The magnetic susceptibility of the compound obeys the Curie-Weiss Law in the range from 77 to 298°K with $\theta = 35^\circ$. The crystals are orthorhombic with unit-cell dimensions: $a = 8.16$, $b = 16.81$, $c = 5.73 \text{ \AA}$, $V = 785.4 \text{ \AA}^3$. The geometric arrangement of the atoms is illustrated. Binding energies for the compound are discussed.

66-7. Blinc, R., E. Pirkmajer, J. Slivnik, and I. Zupančič

NUCLEAR MAGNETIC RESONANCE AND RELAXATION OF HEXAFLUORIDE MOLECULES IN THE SOLID, *J. Chem. Phys.* **45**, 1488 (1966).

The ^{19}F magnetic resonance absorption spectra and spin-lattice relaxation times of polycrystalline UF_6 , PuF_6 , WF_6 , OsF_6 , PtF_6 , MoF_6 , and XeF_6 have been studied as a function of temperature and magnetic field. In all investigated metal hexafluorides the chemical shifts were found to be quite large, exceeding the dipole-dipole broadening in the solid and allowing an unambiguous determination of the tetragonal distortion of the hexafluoride octahedra in the low-temperature orthorhombic phase. The fluorines can, thus occupy either axial or equatorial sites. The chemical shifts of the axial and equatorial fluorines (σ_{axial} = -5350 ppm, $\sigma_{\text{equatorial}}$ = -2800 ppm) with respect to HF, and the anisotropies of the ^{19}F screening tensors in PtF_6 , $|\sigma_{||} - \sigma_{\perp}|_{\text{a}} = 1300 \pm 100 \text{ ppm}$ and $|\sigma_{||} - \sigma_{\perp}|_{\text{e}} = 1380 \pm 100 \text{ ppm}$ seem to be the largest of all known fluorine compounds. A slow, thermally activated motion in which each fluorine atom is alternatively axial and equatorial, and which consists of a hindered rotation and subsequent distortion of the octahedron in the crystalline field of its neighbors, produces at higher temperatures a coalescence of the spectrum into a single, narrow line.

The same fluorine motion was found to influence the spin-lattice relaxation both by a direct modulation of the resonance fields due to anisotropic chemical-shift tensors as well as by a modulation of the dipole-dipole coupling. The solid-solid transitions to the cubic phase in PtF_6 , WF_6 , MoF_6 , were found to be accompanied by a very sharp increase in T_1 and a lowering of the activation energy for molecular motion.

66-8. Chernick, C. L., and J. G. Malm

XENON HEXAFLUORIDE, *Inorg. Syn.* **8**, 258-60 (1966) (Eng.).

The preparation is similar to that of XeF_4 with the exception that the F-Xe mole ratio is increased to 20:1 and the mixture heated to 300°C for 16 hr. A larger vessel is required. XeF_4 is a colorless solid, stable at room temperature, with a vapor pressure of ~30 mm at 25°C. 4 references.

66-9. Claassen, Howard H., and Henry Selig

VIBRATIONAL SPECTRA OF VANADIUM PENTAFLUORIDE, *J. Chem. Phys.* **44**, 4039 (1966).

The infrared spectrum of VF_5 vapor has been studied from 140 to 4000 cm^{-1} . The Raman spectrum has been obtained for the vapor and for the liquid at various temperatures. The spectra indicate a D_{3h} symmetry for the molecule. Fundamental vibrational frequencies observed are: a_1 , 719 and 608; a_2' , 784 and 331; e' , 810,

282, and (~ 200); e'' , 350; all in cm^{-1} . Approximate bond-stretching force constants for a modified Urey-Bradley potential function are: $K_r = 5.51 \text{ Mdyn/\AA}$ and $K_d(\text{axial}) = 3.94 \text{ Mdyn/\AA}$. The Raman spectra show that monomeric molecules are in low concentration in the room-temperature liquid but constitute the main component in the liquid at temperatures above 100°C .

66-10. Cohen, B., and R. D. Peacock

PROPERTIES OF XENON FLUORIDE ADDUCTS, *J. Inorg. Nucl. Chem.* **28**, 3056-57 (1966).

The behavior of XeF_2 and XeF_4 mixed with SbF_5 is rather complex. A yellow crystalline $\text{XeF}_2 \cdot 2\text{SbF}_5$ is observed, but in excess SbF_5 , the NMR signals suggest possible ionic character and only one type of fluorine bonded to xenon. ESR signals and the intensity of a green color in solution are weak with purified XeF_2 ; are observed with XeF_2 - XeF_4 mixtures; and may involve Xe(III) . A weak NMR pattern in the mixture and an easily decomposed white solid may be attributed to the presence of an Xe(IV) species such as $\text{XeF}_4 \cdot 2\text{SbF}_5$.

66-11. Coulson, C. A.

FORCE FIELDS IN KrF_2 AND XeF_2 , *J. Chem. Phys.* **44**, 468-9 (1966).

A possible simple explanation is given of the different signs of the bond-bond interaction constants f_{rr} for the vibrations of KrF_2 and XeF_2 . The magnitude and sign of f_{rr} are related to the ionization potential of the central rare-gas atom and the net charge distribution in the molecule. In KrF_2 the negative sign may be due to the greater weight of a no-bond structure in a resonance description.

66-12. Falconer, W. E., and W. A. Sunder

THE PREPARATION OF XENON DIFLUORIDE BY THE STATIC THERMAL METHOD, *J. Inorg. Nucl. Chem.* **29**, 1380-81 (1966).

A 30% excess of xenon at 400°C yields relatively pure XeF_2 .

66-13. Gavin, Robert Michael, Jr.

EFFECTS OF ELECTRON CORRELATION IN X-RAY DIFFRACTION AND AN ELECTRON DIFFRACTION STUDY OF XeF_4 , USAEC Report IS-T-93, May 1966, 98p.

The theory of X-ray diffraction by gas atoms was examined from the standpoint of one- and two-electron operators. Electron-nuclear $D(r)$ and electron-electron $P(r)$ radial distribution functions for some simple systems were investigated. A comparison of distributions calculated from both correlated and uncorrelated wave functions indicated that $P(r)$ functions are sensitive to the inclusion of electron correlation in the wave function, whereas $D(r)$ functions are not. As a consequence, the total scattered intensity I_{tot} , which is related to $P(r)$, is sensitive to effects of electron correlation whereas the elastic intensity, which is related to $D(r)$, is not. For helium-like systems, the shifts in $P(r)$ and I_{tot} due to electron correlation follow a regular trend with atomic number. A simple scheme for predicting these correlation shifts for more complex atoms was derived from the trends

noted. Correlation shifts in $P(r)$ and I_{tot} for the beryllium atom were predicted and the results compared with shifts calculated from correlated and uncorrelated wave functions. Agreement between predicted and calculated shifts was reasonably good. Radial distribution functions $P(r)$ for neon and argon were derived from experimental X-ray intensities. The resulting distribution functions were used to calculate electron-electron potential-energy values V_{ij} . The V_{ij} for neon and argon calculated from the experimental data are 1.12 and 1.40 a.u., respectively. Corresponding values of 1.20 and 1.36 a.u. were obtained from Hartree-Fock wave functions. The $P(r)$ functions compared favorably with those calculated from existing wave functions, but experimental uncertainties were large enough to obscure effects of electron correlation. The structure of XeF_4 was investigated utilizing the sector-microphotometer method of electron diffraction. Results of the study indicated that the molecule is not a regular octahedron. The mean XeF bond length was $1.887 \pm 0.005 \text{ \AA}$, and the mean amplitude of vibration was $0.070 \pm 0.020 \text{ \AA}$. The nature of the distortion from O_h symmetry is described. The fluorines on one side of the molecule are pushed apart and this deformation compresses the fluorines together toward the other side of the molecule. Three models, with symmetries C_{3v} , C_{2v} , and C_s , containing distortions of this form provide acceptable fits of the experimental data.

66-14. Groz, P., I. Kiss, A. Revesz, T. Sipos

ON THE PREPARATION OF XeF_2 , *J. Inorg. Nucl. Chem.* **28**, 909-10 (1966).

A mixture of F_2 and Xe gas, both of 99.9% purity, was used to prepare XeF_2 . The gases were heated in a reactor that was filled with small nickel plates that could be heated by a resistance furnace to 600°C . The gas was circulated under pressure by means of a Teflon fan, and the product was frozen out in a trap kept below 0°C . The product consisted of well-shaped colorless crystals of the monoclinic system that melted at $130 \pm 0.6^\circ\text{C}$. The product was analyzed by different methods. The mass spectra of the unrefined crystals and a sublimated product are shown. The results seemed to confirm the assumption of Malm *et al.* that some of the chemical properties previously described are more characteristic of XeF_2 than of XeF_4 . The chemical and physical properties in various solutions at low temperatures, and radiation effects on the xenon fluorides, were determined. The gases evolved on irradiation in a quartz tube were mainly D_2 , Xe , and SiF_4 .

66-15. Gunn, Stuart R.

THE HEAT OF FORMATION OF KRYPTON DIFLUORIDE, *J. Am. Chem. Soc.* **88** (1966).

KrF_2 decomposes slowly at 25°C , rapidly at 93°C . The vapor pressures are 10 ± 1 , 29 ± 2 , and $72 \pm 3 \text{ Torr}$ at -15.5 , 0.0 and 15.0°C , respectively; $\Delta H_{\text{subl}} = 9.9 \text{ kcal/mole}$, $\Delta H_f^\circ \text{KrF}_2(g) = 13.7 \text{ kcal/mole}$.

66-16. Hedberg, Kenneth, Steven H. Peterson, R. Robert Ryan, and Bernard Weinstock

ON THE STRUCTURE OF GASEOUS XeF_6 , J. Chem. Phys. **44**, 1726 (1966).

A comparative study was made of XeF_6 and TeF_6 molecular structures by electron diffraction. The XeF_6 sample (>99% pure) was prepared by direct fluorination of xenon at high pressures. The diffraction experiments were made at nozzle temperatures of about 22°C at a camera distance of 25 cm using 0.06-Å electrons and a ν^3 rotating sector. Exposure times were 1 to 4 min. Microphotometric data from photographic plates for each compound are presented. The differences in shapes of the two curves proved that the two molecules are of different structure. The preliminary results strongly supported the conclusion that XeF_6 is not a regular octahedron.

66-17. Holloway, John H.

SYNTHESES OF XENON DIFLUORIDE BY EXPOSURE OF XENON-FLUORINE MIXTURES TO DAYLIGHT AT ROOM TEMPERATURE, Chem. Comm., **22** (1966).

Mixtures of xenon and excess fluorine when sealed in Pyrex glass containers and exposed to sunlight yield crystals of xenon difluoride.

66-18. Holloway, John H.

THE PHOTOCHEMICAL REACTION OF XENON WITH FLUORINE AT ROOM TEMPERATURE: A DEMONSTRATION OF THE REACTIVITY OF XENON, J. Chem. Educ. **43**, 202-3 (1966).

Products of the photochemical reaction between xenon and fluorine in Pyrex bulbs at room temperature and atmospheric pressure and in diffuse daylight or bright sunlight, were studied. Previous experiments showed that, when fluorine is present in excess, although xenon tetrafluoride is produced, it is not the inevitable product of the reaction. Various mixtures of xenon and fluorine were allowed to react in a Pyrex bulb, and mass spectra of the least volatile samples in the bulb showed the fragmentation pattern characteristic of xenon difluoride. Infrared spectra of the vapor phase of the least volatile species present in the bulbs showed the characteristic peaks associated with xenon difluoride. No peaks corresponding with those of other known xenon fluorides or oxide fluorides were observed. The evidence thus shows that xenon difluoride is the only xenon-containing product of the reaction.

66-19. Hoppe, R.

MADELUNG CONSTANTS, Angew. Chem. Intern. Ed. Eng. **5**, 95-106 (1966). Original article in German, Angew. Chem. **78**, 52-63 (1966).

Madelung constants are simple numbers which depend on the type of structure investigated. They are needed for the calculation (using the Born-Haber cycle) of lattice energies and enthalpies of formation of ionic compounds. Each Madelung constant is the sum of partial Madelung constants which represent the contributions of the individual ions to the total lattice energy. The partial Madelung constants depend on the ionic charge and, clearly though not stringently, on the coordination number. On the other hand, each Madelung constant can be represented by a sum of

Madelung constants for related simple primitive AB structures. Surprisingly, these Madelung constants are numerically interrelated in a simple manner, and are related to the partial Madelung constants of interstitial sites. Madelung constants of parameter-dependent structures (e.g., of the rutile or anatase type) and their variations with the structure-determining quantities are of particular interest. Madelung constants also yield information in the case of complex compounds and--surprisingly--of non-metal compounds (e.g., XeF_2 , XeF_4 , XeF_6 , XeF_3 , XeF_5).

66-20. Jaselskis, Bruno, and R. H. Krueger

TITRIMETRIC DETERMINATION OF SOME ORGANIC ACIDS BY XENON TRIOXIDE OXIDATION, Talanta **13**, 945-9 (1966).

Aqueous xenon trioxide in acidic or neutral solutions oxidized carboxylic acids quantitatively to carbon dioxide and water. Micro and semimicro amounts of carboxylic acids may be determined by the iodometric titration of the excess of xenon trioxide remaining in the reaction mixture. The optimum time and temperature for the reaction depend on the structure of the acid; dicarboxylic and hydroxycarboxylic acids react faster than corresponding monocarboxylic acids. Oxalic and polyhydroxy acids are oxidized within 20 min at room temperature while acetic, maleic, succinic, malonic acids require 2 hr at 40°C. Carboxylic acids in amounts less than 100 μg are determined with a coefficient of variation of 4%, which decreases to 1% for amounts over 250 μg .

66-21. Jaselskis, Bruno, T. M. Spittler, and J. L. Huston

PREPARATION AND PROPERTIES OF MONOCESIUM XENATE (CsHXeO_4), J. Am. Chem. Soc. **88**, 2149 (1966).

The reaction of XeO_3 with aqueous CsOH in the presence of fluoride ion yields white crystals which have been shown to be CsHXeO_4 . The existence of this compound has been checked by x-ray and infrared spectroscopy, and determination of the oxidation state of the xenon. CsHXeO_4 is stable in air and is much more stable than XeO_3 . Attempts to prepare rubidium xenate in a similar manner yield mixed salts containing Xe(VI) and Xe(VIII) .

66-22. Jaselskis, Bruno, and J. P. Warriner

TITRIMETRIC DETERMINATION OF PRIMARY AND SECONDARY ALCOHOLS BY XENON TRIOXIDE OXIDATION, Anal. Chem. **38**, 563-4 (1966).

A precise titrimetric method, employing xenon trioxide, for determination of primary and secondary alcohols in aqueous solutions is described. The solution of xenon trioxide is added to the aqueous alcohol, and the reaction, whose products are carbon dioxide and xenon gas, is allowed to proceed for 2 hr at room temperature, and the excess xenon trioxide is titrated iodometrically. The range of hydroxyl concentrations over which this method can be applied includes both the macro- and semimicro-analytical regions. Methanol, ethanol, and 2-propanol can be determined in amounts as low as 30, 25, and 25 μg with a relative standard deviation of 4% at the 100- μg level, the relative standard deviation falls below 1%.

66-23. Johnson, B. F. G., N. L. Paddock, and M. J. Ware

THE TYPICAL ELEMENTS. *Annu. Rep. Progr. Chem.* (Chem. Soc. London) 62, 132-66 (1965) (Pub. 1966).

B compounds; P and S chemistry; adducts and complexes; instrumentation in determining bonding and structure; purification of Cs by solvent, extraction; the isolation of NO^+NO_3^- or of $\text{HNO}_3\cdot\text{HClO}_4$; identification of a graphitic B_2O_3 ; new derivations of the CF_3 radical; establishment of XeF_2 under electrical discharge; and of $\text{O}_2^{\cdot-}$, In^{2+} , Tl^{2+} , TiCl_4^- , and other ionic species are reviewed. 653 references.

66-24. Kettle, S. F. A.

REACTION OF XENON WITH CHLORINE, *Chem. Ind.* (London) 1966(44), 1846.

Cl and Xe sealed in a high-pressure glass tube were allowed to stand at room temperature for a few days. The inside of the tube became slightly opalescent, and a few needlelike crystals were attached to the glass surface. On freezing the Cl and allowing it to melt slowly, it was sometimes possible to see more needles at the bottom of the liquid. The reaction products were not due to gases adsorbed on the glass surface, as proved by experiments in an all glass apparatus. The product reacted instantly with KI solution, I being liberated. The colorless crystals are probably XeCl_2 . The deposit on the surface of the glass is probably Xe oxychloride or a chloro salt. It should be possible to prepare large quantities of XeCl_2 in a static system.

66-25. Kirin, I. S., A. N. Murin, V. D. Nefedov, Yu. K. Gusev, and G. G. Selikhov

PRODUCTION OF XeO_3 BY β DECAY OF ^{131}I IN HIO_3 AND I_2O_5 COMPOSITION, *Radiokhimiya* 8, 104-9 (1966). (In Russian.)

The possibility of the formation of the trioxide of ^{131m}Xe during the β decay of ^{131}I in the compounds I_2O_5 and HIO_3 was examined. It was found that the introduction of XeO_3 as a carrier leads to an increase in the yield of the bound xenon.

66-26. Kuhn, Gerard

LES COMPOSES CHIMIQUES DES GAZ RARES, (Chemical Compounds Formed by the Rare Gases) CEA-Bib-58 (Jan 1966) 38p.

A review is presented on the properties of rare gas atoms and the preparation and properties of all known compounds up to January 1, 1965. Different theories attempting to explain the existence of these compounds were examined and some applications are described. (139 references.)

66-27. MacKenzie, D. R., and J. Fajer

SYNTHESIS OF NOBLE GAS COMPOUNDS BY PROTON BOMBARDMENT, *Inorg. Chem.* 5, 699-700 (1966).

The techniques for preparing noble gas compounds using 10-MeV proton beams were studied. Gas mixtures of krypton or xenon and fluorine readily reacted on proton bombardment to yield krypton and xenon fluoride. A 1-hr irradiation, at 5 μA , yielded ~ 1 g of KrF_2 . The G values for the formation of the fluorides ranged from 1 to 1.5 molecules/100 eV. KrF_2 was

prepared at temperatures as high as -60°C . The yields decreased with increasing temperature. Attempts to prepare the previously reported KrF_4 were unsuccessful. Even at high fluorine to krypton ratios (9:1) only KrF_2 was detected. Also, attempts to prepare XeF_8 by the analogous reaction of XeF_4 with fluorine were unsuccessful. The window of the cell blew out during bombardment of oxygen and xenon at -196°C . The reaction and the explosion were presumably due to the unstable XeO_3 . All the noble gas fluorides previously reported were synthesized, with the exception of KrF_4 and XeF_8 .

66-28. Malm, J. G., and C. L. Chernick

XENON TETRAFLUORIDE, *Inorg. Syn.* 8, 254-8 (1966).

A 90% yield of XeF_4 is obtained when 5 parts F and 1 part Xe are heated in a closed system at 400°C for 1 hr. The pressure obtained is about 7 atm. XeF_4 is a colorless crystal, solid at 25°C with a vapor pressure of 2.5 mm and is soluble in anhydrous HF.

66-29. Marcus, V., and Donald Cohen

AMERICIUM(III) PERXENATE, *Inorg. Chem.* 44, 1740 (1966).

Americium perxenate has been prepared by precipitation from basic solutions of Am(III). The compound is orange and shows the characteristic absorption bands of Am(III) in the visible and near-infrared regions, as well as the characteristic infrared absorption at $650\text{--}680\text{ cm}^{-1}$ for the Xe-O vibration in perxenate. The compound is highly hydrated and has the stoichiometric composition $\text{Am}_4(\text{XeO}_6)_3\cdot 40\text{H}_2\text{O}$. Its solubility in water is $4.6 \times 10^{-5}\text{ M}$. The compound dissolves in acid to form Am(VI) and Am(V).

66-30. Margraff, R., and J. P. Adloff

CHEMICAL TRANSFORMATIONS ACCOMPANYING THE IRRADIATION OF SOLID COMPOUNDS OF XENON IN A NEUTRON FLUX, *Radiochim. Acta.* 6, 138-43 (Dec 1966). (In French.)

Irradiation of xenon led to several radioisotopes, allowing investigation of chemical effects of (n,γ) reactions, isomeric transition, and electron capture. Solid samples of XeF_2 , XeF_4 , and $\text{Ba}_2\text{XeO}_6\cdot 2\text{H}_2\text{O}$ were irradiated in a neutron flux. Retention of radioxenon amounted to 93% in the difluoride; total retention approached 100% in the tetrafluoride, but two-thirds of the radioxenon appeared as XeF_2 . No isotope effect was found. In perxenate, 30% of xenon remained chemically bound. The isomeric transition $^{131m}\text{Xe} \rightarrow ^{131}\text{Xe}$ in XeF_4 did not lead to significant release of xenon. In the same matrix, ^{125}I daughter product of ^{125}Xe , appeared mainly as IF_5 .

66-31. Margraff, R., and J. P. Adloff

SZILARD-CHALMERS EFFECTS IN SOLID XENON COMPOUNDS, 11p. (CONF-660431-3). ORAU, Gmelin, AED-CONF-66-120-3.

From Symposium on Hot Atom Chemistry, Lafayette, Indiana, April 1-2, 1966.

The behavior of solid xenon fluorides was investigated in relation to isotopes that arise from in-pile irradiation of natural xenon, separation of free xenon from the fluorides, and determination of the nature of the bound

xenon (physical and chemical retention) after irradiation. An unexpectedly high fraction of radioxenon remained chemically bound after the irradiation. The retention was nearly quantitative in the tetrafluoride, and quite independent of irradiation time and neutron flux in the limits investigated. The chemical nature of the retained radioxenon was elucidated from the results of the hydrolysis reactions of the different fluorides. The retention of the radioxenon in an irradiated perxenate salt is also discussed.

66-32. Meinert, Hasso

FORMATION OF XENON DICHLORIDE, *Z. Chem.* **6**, 71 (1966). (In German.)

Colorless crystals are formed when an electric discharge is passed through an equimolar mixture of Xe, F₂, and SiCl₄ or CCl₄ in a cooled (-80 to -195°C) quartz vessel. Mass-spectrometric examination of the vapor shows peaks corresponding to XeCl, suggesting XeCl₂ as the parent molecule. The crystals can be purified by sublimation under reduced pressure, but they decomposed under high vacuum or at temperatures about +80°C.

66-33. Meinert, Hasso, and Gerhard Gnauck

METHOD FOR PREPARING XENON AND KRYPTON FLUORIDES, East German Patent No. 51, 302, Nov. 5, 1966, 2pp.

A new method for making Xe and Kr fluorides is described wherein CF₂Cl₂ is used to react with Xe or Kr. In an example, Xe or Kr is subjected to a high-frequency discharge by means of external electrodes at 150-200 mA in a quartz vessel containing CF₂Cl₂. The resulting noble gas fluorides are collected in a cooling trap. The unreacted mixture is recirculated.

66-34. Moody, G. J., and H. Selig

NITROSYL FLUORIDE-XENON FLUORIDE COMPLEXES, *Inorg. Nucl. Chem. Letters* **2**, 319-21 (1966).

Complexes are formed between NOF and XeF₆ and XeOF₄. Weight change, infrared absorption, and Raman-spectra observations are interpreted in terms of (NO)₂⁺XeF₈²⁻ and NO⁺XeOF₅⁻ in condensed phases which dissociate completely in the vapor.

66-35. Moody, G. J., and H. Selig

VANADIUM PENTAFLUORIDE COMPLEXES WITH XENON FLUORIDES, *J. Inorg. Nucl. Chem.* **28**, 2429-30 (Oct 1966).

A study of the complexes formed by the VF₅ reaction with XeF₆ and with XeOF₄ was made. The physical properties and infrared spectra of the complexes 2XeF₆·VF₅ and 2XeOF₄·VF₅ are given. Ten of the eighteen known Xe(VI) complexes were examined for overall hydrolysis patterns, and like XeF₆, were found to react with 100% xenon retention.

66-36. Moody, G. J., and J. D. R. Thomas

NOBLE GAS CHEMISTRY, *Rev. Pure and Appl. Chem.* **16**, 1-24 (1966).

A detailed review of the literature after January 1964. 168 references.

66-37. Murin, A. N., I. S. Kirin, V. D. Nefedov, S. A. Grachev, Yu. K. Gusev, N. V. Ivannikova, and V. S. Gusel'nikov

PRODUCTION OF OXYGEN COMPOUNDS OF XENON BY β DECAY OF IODINE ISOTOPES AND STUDY OF THEIR PROPERTIES, *Radiokhimiya* **8**, 449-54 (1966). (In Russian.)

The possibility of using chemical transformations during β decay of iodine isotopes for the synthesis of radioactive xenon trioxide was studied. A method was developed for the investigation of xenon compounds that were formed during the β decay of ¹³¹I and ¹³³I as potassium iodate and periodate.

66-38. Nagarajan, G.

MEAN AMPLITUDES OF VIBRATION, BASTIANSSEN-MORINO SHRINKAGE EFFECT, AND THERMODYNAMIC FUNCTIONS OF KRYPTON DIFLUORIDE, *Acta Phys. Pol.* **29**(6), 831-6 (1966) (Eng.).

The Cyvin method (CA 54, 5235d) employing symmetry coordinates is used to evaluate the mean-square amplitudes of vibration, generalized mean-square amplitudes (mean-square parallel amplitudes, mean-square perpendicular amplitudes, and mean cross products) and mean amplitudes of vibration for the bonded as well as nonbonded atom pairs at 298, 500, and 1000°K for KrF₂ symmetry point group D_{∞h}. The values of Bastianssen-Morino shrinkage effect at these temperatures were calculated from the mean-square perpendicular amplitudes. The statistical thermodynamic functions were computed at 100-2000°K on the basis of a rigid-rotator, harmonic-oscillator model.

66-39. Nefedov, V. D., I. S. Kirin, V. I. Tikhonov, and V. M. Zaitsev

SEPARATION OF NUCLEAR ISOMERS OF XENON-133, *Radiokhimiya* **8**(6), 714-16 (1966) (Russian).

Experiments were made on the separation of nuclear isomers of ¹³³Xe. XeF₄ was irradiated for 5 hr with thermal neutrons at 5 × 10¹³ n/cm²-sec. The irradiated sample was held for 2 days until the short-lived Xe isotopes decayed. The XeF₄ contained ¹³³Xe and ^{133m}Xe and was used for accumulating the isomer in the ground state. The accumulation took place during 4 days at -20°C. Elemental ¹³³Xe was separated by careful recrystallization of the preparation at 50-60°C, then the temperature was again reduced to -20°C. Accumulation was also carried out in aqueous solutions of XeO₃ obtained in the hydrolysis of irradiated XeF₄ in 0.002N H₂SO₄. Then, He was passed through the solution to eliminate Xe gas. Accumulation took place during 4 days, then He was again passed through the solution, and Xe was collected on activated carbon at -78°C. Xe was determined by measuring the relative intensity of the γ emission of both isomers on a 100-channel γ spectrometer. As a result of the isomer transition the gas phase is enriched with the isomer which is in the ground state. The yield of ¹³³Xe in the ground state is not more than 50%. It was not possible to avoid partial chemical decomposition of the Xe compounds. This is shown by a peak in the Xe spectrum belonging to an isomer in the metastable state. 7 references.

66-40. Nefedov, V. D., M. A. Toropova, A. V. Levchenko, and A. N. Mosevich

STUDIES OF CHEMICAL RESULTS OF ^{131}I β DECAY IN THE IODOXYBENZENE, Radiokhimiya **8**, 719-20 (1966). (In Russian.)

Experimental studies showed that $^{131}\text{mXeO}_3$ was formed during ^{131}I β decay in iodoxybenzene diluted with acetic and perchloric acid solutions. An additional confirmation of XeO_3 formation was found by observing accumulations in alkaline iodoxybenzene solutions, which revealed that all xenon formed was in a free state, in good agreement with published data about the unstable state of XeO_3 in alkaline media.

66-41. Ogden, J. S., and J. J. Turner

THE HYDROLYSIS OF XENON TETRAFLUORIDE AT -80° , Chem. Comm. **19**, 693-4 (1966).

XeF_4 and H_2O vapors react at -80°C to yield a bright yellow deposit. No ESR signal was observed. IR bands were found at 747, 520, and 490 cm^{-1} . Using D and ^{18}O substitutions the IR spectrum was interpreted as arising from XeOF_2 . The 747-cm^{-1} band is an XeO stretch (force constant of 4.7 mdynes/\AA), and the 520- and 470-cm^{-1} bands are the XeF symmetrical stretch and asymmetrical stretch, respectively.

66-42. Peacock, R. D., H. Selig, and I. Sheft

COMPLEX COMPOUNDS OF XENON HEXAFLUORIDE WITH THE ALKALI FLUORIDES, J. Inorg. Nucl. Chem. **28**, 2561-7 (1966).

The complex salts CsXeF_7 , RbXeF_7 , C_2XeF_8 , and Rb_2XeF_8 have been prepared and characterized, and evidence is presented for the existence of K_2XeF_8 and Na_2XeF_8 . The decomposition pressures of CsXeF_7 and RbXeF_7 have been measured. The liquid density of XeF_6 has been determined over the range $50\text{-}76^\circ\text{C}$, but attempts to measure the conductance of a solution of CsXeF_7 in XeF_6 have not been successful.

66-43. Pullen, Kent E., and George H. Cady

THE REACTION OF XENON HEXAFLUORIDE WITH STANNIC FLUORIDE, Inorg. Chem. **5**, 2057-9 (1966).

Excess XeF_6 was treated with SnF_4 to yield $4\text{XeF}_6\cdot\text{SnF}_4$, a strong oxidizing and fluorinating agent. When heated above 50°C under vacuum $4\text{XeF}_6\cdot\text{SnF}_4$ decomposes with a loss of XeF_6 .

66-44. Ruby, S. L., and H. Selig

MÖSSBAUER STUDY OF Kr^{83} IN THE COMPOUND KrF_2 , Phys. Rev. **147**, 348-54 (1966).

The compound KrF_2 has been studied by use of the techniques of Mössbauer spectroscopy. The results are that (a) the interaction energy is $e^2qQ_g = 130 \pm 4\text{ mm/sec} = 960 \pm 30\text{ mHz}$, (b) the ratio of the nuclear quadrupole moment of the excited state to that of the ground state is $R = Q_e/Q_g = 1.70 \pm 0.02$, and (c) the isomer shift referred to atomic krypton is $1.50 \pm 0.10\text{ mm/sec}$. These results are interpreted as supporting the infrared, Raman, and NMR results which other groups had previously obtained for this compound and as confirming the earlier conclusions reached with the analogous compound XeF_2 . The quadrupole moment of the first excited state of ^{83}Kr is

found to be $0.459 \pm 0.006\text{ b}$, and the fractional decrease in charge radius between the first excited state and the ground state is approximately 4×10^{-4} .

66-45. Seery, Daniel J., and Doyle Britton

SHOCK WAVES IN CHEMICAL KINETICS. FURTHER STUDIES IN THE DISSOCIATION OF FLUORINE, J. Phys. Chem. **70**, 4074-6 (1966).

The dissociation of F_2 proceeds more slowly in Ar than would be expected by comparison to other halogens. Kr does not affect the dissociation rate in Ar. With Xe the dissociation rate is affected and at least one stable, colored Xe-F species is formed at $1100\text{-}1600^\circ\text{K}$.

66-46. Selig, Henry

COMPLEXES OF XENON OXIDE TETRAFLUORIDE, Inorg. Chem. **5**, 183-6 (1966).

XeOF_4 bears a strong resemblance to the halogen fluorides both in physical properties and chemical behavior. XeOF_4 is a clear, colorless liquid freezing at -46.2°C . Its electrical conductivity at 24°C is $1.03 \times 10^{-5}\text{ ohm}^{-1}\text{ cm}^{-1}$, and its dielectric constant is 24.6 at 24°C . It is miscible with anhydrous HF, but its conductivity is not enhanced in such a solution. The addition of CsF or RbF to XeOF_4 increases its conductivity markedly. XeOF_4 forms a series of addition compounds with the heavier alkali fluorides. The following complexes were isolated: $\text{CsF}\cdot\text{XeOF}_4$, $3\text{RbF}\cdot 2\text{XeOF}_4$, and $3\text{KF}\cdot\text{XeOF}_4$. No reaction occurred with NaF. Thermogravimetric studies showed that a number of intermediates are formed before final decomposition to the alkali fluorides. XeOF_4 reacted with SbF_5 to form a complex of composition $\text{XeOF}_4\cdot 2\text{SbF}_5$. A reaction also occurred with AsF_5 at -78°C , but the complex was unstable at room temperature.

66-47. Selig, H. H., L. A. Quarterman, and H. H. Hyman

RAMAN SPECTRUM AND HYDROLYSIS STUDIES ON HYDROGEN FLUORIDE SOLUTIONS OF XENON OXIDE TETRAFLUORIDE, J. Inorg. Nucl. Chem. **28**, 2063-5 (1966).

Previous studies indicated the possible existence of the compound xenon dioxide difluoride in an incompletely hydrolyzed sample of xenon hexafluoride. An attempt was made to characterize this compound through its Raman spectrum. It was found that the Raman spectrum of xenon oxide tetrafluoride as a solute in hydrogen fluoride is similar to that of pure liquid oxide tetrafluoride. When a small amount of water was added to the solution, no new hydrogen fluoride soluble species was observed. An unstable white precipitate was formed, probably xenon trioxide. No evidence was found for the existence of xenon dioxide difluoride.

66-48. Selig, H., and F. Schreiner

MAGNETIC SUSCEPTIBILITY OF XeF_6 , H. Chem. Phys. **45**, 4755 (1966).

Samples of purified XeF_6 show temperature-independent diamagnetism from 77 to 325°K .

66-49. Streng, L. V., and A. G. Streng

PHOTOCHEMICAL FORMATION OF KRYPTON DIFLUORIDE FROM KRYPTON AND FLUORINE OR OXYGEN DIFLUORIDE, *Inorg. Chem.* **5**, 328-9 (1966).

Photochemical formation of KrF_2 from equimolar mixtures of Kr and F_2 or Kr and OF_2 and exposing them to sunlight for 5 weeks in dry glass flasks at room temperature and at a total pressure of 1 atm absolute is reported. When the same flasks with Kr- F_2 or Kr- OF_2 mixtures were kept in the dark for the same period of time, there was no formation of krypton fluoride crystals. The products were analyzed by thermal decomposition and measuring and analyzing the gas evolved.

66-50. Trofimov, A. M., and Yu. N. Kazankin

CLATHRATE COMPOUNDS OF P-CRESOL WITH INERT GASES, *Radiokhimiya* **8**(6), 720-3 (1966) (Russian).

The clathrate compound of p-cresol with Kr was obtained, and equilibrium pressures for the system were determined at 5-35°C. From these data, the heats of formation of compounds from solid and liquid p-cresol were calculated at 4.8 and 21.5 kcal/mole, respectively. Physicochemical analysis indicated that the formula for the compound could be expressed as $\text{Kr} \cdot 6(\text{C}_7\text{H}_8\text{O})$. The system Xe-(Rn)-p-cresol also was studied, and a determination was made of the fractionation constants of Rn in isomorphous cocrystallization with Xe in the clathrate p-cresol compound, at 20 and 30°C. Rn also forms clathrate compounds with p-cresol, in a manner similar to Xe and Kr.

66-51. Volavsek, B.

MAGNETIC SUSCEPTIBILITY OF XENON HEXAFLUORIDE, *Monatsh. Chem.* **97**(5), 1531-2 (1966) (German).

XeF_6 has been found to be diamagnetic with magnetic susceptibility $\chi_M = -44.5 \times 10^{-6} \text{ cm}^3/\text{mole}$ from measurements between 201 and 273°K.

66-52. Weaver, Clayton Fred

KINETICS OF FORMATION OF XENON FLUORIDES, UCRL-17169 (Sept 1966).

The temperature dependence of the near-ultraviolet region of the absorption spectra of F_2 and XeF_2 was determined to 400°C in fluorinated nickel cells with calcium fluoride windows. That of XeF_4 was determined to 250°C. This spectral information was used to study the kinetics of the formation of XeF_2 and XeF_4 in the same temperature regions and in the same nickel cells. Experimental conditions were chosen to cause the reactions to terminate at XeF_2 or XeF_4 . With a total pressure of reactants in the 10 to 40 mm range and Xe to F_2 ratios of 10 or more, the reaction $\text{Xe} + \text{F}_2 \rightarrow \text{XeF}_2$ occurred. Under these conditions the reaction was zero order in Xe and first order in F_2 over the temperature range from 190 to 400°C. With total reactant pressures of 10 to 20 mm and F_2 to Xe ratios of 16 or more, the reaction $\text{Xe} + 2\text{F}_2 \rightarrow \text{XeF}_4$ occurred with XeF_2 as an intermediate. Under these conditions in the temperature range from 190 to 250°C, the formation of XeF_2 was zero order in F_2 and first order in Xe, just the opposite of the results above. The formation of XeF_4 was zero order in F_2 and first order in XeF_2 . The

reactions were heterogeneous, even though they were very reproducible. The activation energies were uniformly low, ranging from 12.8 to 15.7 kcal/mole. A mechanism involving adsorption and dissociation of F_2 on the NiF_2 surface is proposed.

66-53. Weeks, James L., and Max S. Matheson

XENON DIFLUORIDE, *Inorg. Syn.* **8**, 260-4 (1966).

Xe and F react to form XeF_2 , m.p. $\sim 140^\circ\text{C}$, when irradiated with UV light at 2300-3500 Å. When it is trapped at -87°C , essentially pure product is obtained. XeF_2 dissolves in H_2O giving undissociated XeF_2 , half-life 7 hr at 0°C , eventually decomposing to Xe and HF.

66-54. Weinstock, Bernard, E. Eugene Weaver, and Charles P. Knop

THE XENON-FLUORINE SYSTEM, *Inorg. Chem.* **5**, 2189 (1966).

Equilibrium constants have been obtained in the Xe- F_2 system in the temperature range 250-500°C. The data show that only three binary fluorides, XeF_2 , XeF_4 , and XeF_6 are present. There is no evidence for the existence of XeF_3 at 250°C and up to 500 atm of F_2 . A preparation of pure XeF_4 is described. A molecular weight determination, some infrared measurements, and vapor pressure data obtained with this sample are reported. Values for the thermodynamic properties of formation of XeF_2 , XeF_4 , and XeF_6 were derived from the equilibrium-constant data. The average value of the two missing vibrational modes of XeF_4 was evaluated to be $246 \pm 10 \text{ cm}^{-1}$ from an analysis of the equilibrium constant and molecular data. Thermodynamic properties of XeF_2 and XeF_4 were calculated from molecular data. The value of S° for XeF_4 at 25°C is 75.6 cal $\text{mole}^{-1} \text{ deg}^{-1}$, in agreement with a value of 75.3 cal $\text{mole}^{-1} \text{ deg}^{-1}$ calculated from calorimetric data and the heat of sublimation. A number of molecular models for XeF_6 were examined in terms of their consistency with the equilibrium-constant data. A definite choice among the various models was not possible, but the analysis favored a low symmetry for XeF_6 . Values of S° for XeF_4 at 25°C were derived for each model and may be useful to help determine the symmetry of XeF_6 when calorimetric data become available. The average bond energy of XeF_2 is 31.0 kcal and that of XeF_4 is 30.9 kcal. For XeF_6 the average bond energy is 29.7 kcal, so that the average energy for forming the last two bonds in XeF_6 is 27.3 kcal.

66-55. Willett, Roger D.

A COMMENT ON THE BONDING IN XeF_6 , *Theor. Chim. Acta* **6**(2), 186-8 (1966).

Molecular orbitals are given for XeF_2 , XeF_4 , and XeF_6 . The possible distortion of the latter and the contribution of a small amount of d orbital mixing are discussed.

66-56. Yeranov, Walter A.

SEMI-EMPIRICAL MOLECULAR ORBITAL ENERGY LEVELS OF XeF_4 , *Mol. Phys.* **11**, 85-92 (1966).

Using recently published analytical SCF wave functions for xenon, the one-electron molecular-orbital energies of XeF_3 were redetermined in the Wolfsberg-Helmholz semi-empirical approximation. Unlike similar previous investigations, the study considered ligand-ligand overlap, and used the recently proposed reciprocal

mean for the semi-empirical evaluation of the resonance integrals. The results coincided with observed electronic transitions in the far UV spectrum of XeF₄.

66-57. Yeranov, Walter A., and Nicholas W. Winter
SUGGESTED SEMIEMPIRICAL MOLECULAR
ORBITAL SCHEMES FOR XENON TETROXIDE, *Bull.*
Soc. Chim. Belges **75**, 116-26 (1966).

One-electron molecular-orbital energies have been determined for xenon tetroxide, in three approximations. Two distinct classes of bonding can be formulated. One class has a triplet ground state, and hence the possibility of exhibiting electron-spin resonance. The other has a singlet ground state, and one would not expect resonance. Experimental evidence is not yet available to distinguish between the theories.

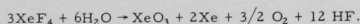
1967

67-1. Allamagny, P., and M. Langignard

VARIATION OF OXIDIZING POWER OF AQUEOUS
XENON TRIOXIDE SOLUTIONS IN THE PRESENCE
OF XENON DIFLUORIDE, *Bull. Soc. Chim. de France*,
1967, 3630-3 (French).

The oxidizing power of acid solutions of XeO₃ obtained on hydrolysis of XeF₄ decreases in the presence of XeF₂. The decrease is a function of the concentration of XeF₂, XeO₃, and of the pH of the solution, and XeO₃ is not simply consumed in a well-defined reaction.

The hydrolysis of XeF₄ follows the equation,



The resulting acid solution of XeO₃ is stable only if the XeF₄ is quite free from XeF₂.

67-2. Allamagny, Paul, and Michel Langignard

THERMAL DECOMPOSITION OF XENON TRIOXIDE,
C. R. Acad. Sci., Paris, Ser. C **264**(23), 1844-6 (1967).

A smooth thermal decomposition was demonstrated over the temperature range 40-140°C at 0-25 mm. Only Xe and O₂ were found.

67-3. Appelman, Evan H.

THE NATURE OF AQUEOUS DIVALENT XENON,
Inorg. Chem. **6**, 1268-9 (1967).

The absence of significant electrical conductivity and ¹⁹F exchange with F⁻ in aqueous solutions of xenon difluoride confirm the existence of the molecule itself as the principal species.

67-4. Appelman, Evan H.

THE REACTION OF XENON DIFLUORIDE WITH
WATER AND WITH XENON TRIOXIDE, *Inorganic*
Chemistry **6**, 1305 (1967).

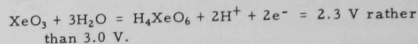
In 0.01 M HClO₄ xenon difluoride oxidizes water with a first-order rate constant of $4.2 \times 10^{-4} \text{ sec}^{-1}$ at 25°, and with $\Delta H^{++} = 19.6 \text{ kcal/mole}$ and $\Delta S^{++} = -8.1 \text{ eu}$. The reaction is catalyzed by bases and by substances with affinity for fluoride ion. Intermediates in the reaction oxidize benzenesulfonic acid and reduce XeO₃. The reduction of XeO₃ has been studied in detail. The number of XeO₃ molecules consumed per molecule of

XeF₂ varies from zero to 1, depending on the initial ratio of concentrations. Mechanisms are proposed invoking XeO and XeO₂ as intermediates.

67-5. Appelman, E. H., and J. G. Malm

HYDROLYSIS OF XENON HEXAFLUORIDE AND THE
AQUEOUS SOLUTION CHEMISTRY OF XENON, *J. Am.*
Chem. Soc. **89**, 3665 (1967). Correction to *J. Am.*
Chem. Soc. **86**, 2141 (1964).

The electrode potential for



67-6. Bartell, L. S.

EVIDENCE FOR PSEUDO-JAHN-TELLER EFFECT
IN XeF₆, *J. Chem. Phys.* **46**(11), 4530-1 (1967).

Electron-diffraction data for XeF₆ are interpreted on the basis of a model of dynamic distortion symptomatic of a pseudo-Jahn-Teller interaction. Several structural properties of XeF₆ inferred from this interpretation are in agreement with thermodynamic and molecular-beam data.

67-7. Bartlett, Neil, Fred Einstein, D. F. Stewart,
and James Trotter

THE CRYSTAL STRUCTURE OF [XeF₅]⁺ [PtF₆]⁻,
J. Chem. Soc., A (7), 1190-3 (1967).

Crystals of F₁₁PtXe are orthorhombic, with $a = 8.16$, $b = 6.81$, $c = 5.73 \text{ Å}$, $Z = 4$, space group Pmnb. The structure was determined from three-dimensional Patterson and electron-diffraction maps, by using Mo K_α scintillation-counter data, and refined by least-square methods; the final R value is 0.130 for 549 observed reflections. The structure can be formulated as [XeF₅]⁺ [PtF₆]⁻. The [XeF₅]⁺ ion has five F atoms and a nonbonding electron pair in a distorted octahedral arrangement around Xe; in the [PtF₆]⁻ ion, Pt is coordinated octahedrally to six F atoms. Four F atoms from different [PtF₆]⁻ ions form bridges to the Xe atom, with Xe...F distances of 2.52, 2.65, and 2.95 Å, the directions of approach of the F suggesting steric activity of the Xe nonbonding electron pair.

67-8. Beck, M. T., and L. Dózsa

CATALYSIS AND INHIBITION OF THE HYDROLYSIS
OF XENON DIFLUORIDE, *J. Am. Chem. Soc.* **89**,
5713-4 (1967).

The rate of hydrolysis is a minimum in the pH range 4-9. Cations which complex fluoride ion accelerate the reaction according to the stability constants of their monofluoro complexes, $\text{Th}^{4+} > \text{Al}^{3+} > \text{Be}^{2+} > \text{La}^{3+}$.

Fluoride ions, carbonate and hydrogen carbonate and phosphate and hydrogen phosphate ions catalyze hydrolysis, high ionic strength retards reaction.

67-9. Cleaver, Charles S.

XENON FLUORIDES, U.S. Pat. #3,326,638 (1967).

N₂F₂ reacts with xenon at 80-150°C.

67-10. Cleveland, J. M.

KINETICS OF THE REACTION BETWEEN PLUTONIUM(III) AND XENON TRIOXIDE, *Inorg. Chem.* **6**, 1302-5 (July 1967).

The kinetics of the reaction between Pu(III) and XeO₃, according to the equation $6\text{Pu(III)} + \text{XeO}_3 + 6\text{H}^+ \rightarrow 6\text{Pu(IV)} + \text{Xe} + 3\text{H}_2\text{O}$, were studied in perchlorate media by following the rate of disappearance of Pu(III) spectrophotometrically at 600 mμ. The rate law for the reaction is $-d[\text{Pu(III)}]/dt = k[\text{Pu(III)}][\text{XeO}_3]$. The reaction rate was independent of acidity in the 0.5 to 2 M range. From the variation of the reaction rate with temperature, the following thermodynamic quantities of activation at 25°C were calculated: $\Delta H^\ddagger = 15.3 \pm 2.1$ kcal/mole; $\Delta F^\ddagger = 20.2 \pm 0.1$ kcal/mole; $\Delta S^\ddagger = -16.0 \pm 6.9$ eu. The mechanism of the reaction appeared to involve either successive one-electron changes or a two-electron change to form a Pu(V) species other than PuO₂⁺, which then reacts with Pu(III) to form Pu(IV).

67-11. Cleveland, J. M., and G. J. Werkema

PHOTOCHEMICAL OXIDATION OF NEPTUNIUM(V) BY XENON TRIOXIDE, *Nature (London)* **215**, 732-3 (Aug. 12, 1967).

XeO₃ is a strong oxidising agent, with a potential of -1.8 V. Evidence was obtained for a photochemical reaction $6\text{Np(V)} + \text{Xe(VI)} \rightarrow 6\text{Np(VI)} + \text{Xe}$. The experimental technique adopted is described, and all runs were conducted at 60°C to give a conveniently measurable rate. The concentration of Np(V) was followed at 980 mμ, and the several steps of data reduction were evaluated by computer program. Rate constants are tabulated. It was concluded that the reaction is first order in XeO₃ and zero order in Np(V). The rate appeared independent of acidity in the 0.5 to 2 M range. The reaction appears to be photochemical, involving the excited species XeO₃, and formation of this species appears to be the rate-controlling step. The excited species reacts rapidly with the Np(V). Runs conducted outside the spectrophotometer light path did not obey the same rate law; reaction was much slower, and was nonintegral dependent on Np(V), XeO₃, and possibly Np(VI) concentrations. It appears that XeO₃ oxidises by a two-electron change mechanism, and that the oxidation is hindered in cases where only a one-electron change is permissible.

67-12. Code, R. F., W. E. Falconer, W. Klemperer, and I. Ozier

MAGNETIC-FIELD DEFLECTION OF XeF₆, *J. Chem. Phys.* **47**, 4955-8 (1967).

The deflection of a molecular beam of XeF₆ has been measured in an inhomogeneous magnetic field. From the similarity of the deflection of XeF₄ and SF₆ and the difference with the deflection of O₂ it is concluded that gaseous XeF₆ at room temperature does not contain a paramagnetic component greater than ~190 in abundance. This conclusion is not consistent with Goodman's hypothesis that a low-lying ³Tu state of XeF₆ is appreciably populated at room temperature.

67-13. Fadini, A., and A. Müller

CALCULATION OF FORCE CONSTANTS OF THE GENERAL VALENCE FORCE FIELDS OF MOLECULES AND IONS OF THE XY₄ TYPE WITH D_{4h}-SYMMETRY BY THE "NEXT APPROXIMATION PROCESS?" *Mol. Phys.* **12**, 145-8 (1967).

For XeF₄ the literature values taken are:

| | | | |
|------------------------|----------------------|---------------------|----------------------|
| $\nu_1(\text{A}_{1g})$ | 543 cm ⁻¹ | $\nu_6(\text{E}_u)$ | 586 cm ⁻¹ |
| $\nu_3(\text{B}_{1g})$ | 235 cm ⁻¹ | $\nu_7(\text{E}_u)$ | 123 cm ⁻¹ |
| $\nu_4(\text{B}_{2g})$ | 502 cm ⁻¹ | | |

The literature f_γ is 3.00 (mdyn/Å). The calculated values are:

| | | | |
|---------------------|------|--------------------------------|-------|
| f_γ | 3.02 | $f_a - f_{aa}$ | 0.11 |
| $f_{\gamma\gamma}$ | 0.12 | $f_a - f_{aa}$ | 0.07 |
| $f_{\gamma\gamma'}$ | 0.04 | $f_{\gamma a} - f_{\gamma a'}$ | ~0.00 |

67-14. Falconer, W. E., and W. A. Sunder

THE PREPARATION OF XENON DIFLUORIDE BY THE STATIC THERMAL METHOD, *J. Inorg. Nucl. Chem.* **29**, 1380-1 (1967).

A 30% excess of xenon at 400°C yields relatively pure XeF₂.

67-15. Gasner, Earl L., and Howard H. Claassen
RAMAN SPECTRUM OF XENON HEXAFLUORIDE, *Inorg. Chem.* **6**, 1937-8 (1967).

The spectra of the solid, liquid at 54°C and at 92°C and the vapor at 94°C are given. The solid and low temperature liquid are polymeric materials and the degree of association decreases near the boiling point. The vapor is monomeric but the spectrum is different from that of other hexafluoride molecules, particularly in that the highest frequency polarized band is broad while the breathing vibration of a symmetrical hexafluoride should be sharp.

67-16. Gilbert, T. L., and Arnold C. Wahl

SINGLE-CONFIGURATION WAVEFUNCTIONS AND POTENTIAL CURVES FOR THE GROUND STATES OF He₂, Ne₂, AND Ar₂, *J. Chem. Phys.* **47**(9), 3425-38 (Nov. 1, 1967).

Potential energy curves are calculated for He₂, Ne₂, and Ar₂ using single-configuration wavefunctions constructed from molecular orbitals. In one set of calculations the molecular orbitals are chosen to be linear combination of Hartree-Fock orbitals of the separated atoms (the LCAO-MO approximation). In another set of calculations SCF molecular orbitals are obtained by the expansion method (the SCF-MO approximation) with basis functions taken from SCF calculations on the separated atoms. SCF-MO's for He₂ are also calculated with basis functions which have been "optimized" by varying the parameters in the exponents until the total energy is a minimum. Potential curves for these different calculations are compared among themselves and with experiment.

67-17. Gunn, Stuart R.

THE HEAT OF FORMATION OF KRYPTON DIFLUORIDE, *J. Phys. Chem.* **71**(9), 2934-7 (1967).

The heat of decomposition was measured at 93° where decomposition is rapid. After corrections the derived value of ΔH_f° (KrF₂, g) is 14.4 ± 0.8 kcal/mole.

67-18. Gusev, Yu. K., I. S. Kirin, and V. K. Isupov

FORMATION OF XeO₃ DURING β DECAY OF ¹³¹I IN SOME PERIODATE SOLUTIONS, *Radiokhimiya* **2**, 736 (1967). (In Russian.)

Studies were made of chemical reactions taking place during β decay of ¹³¹I in oxygen-containing compounds of seven-valence iodine. Emanation of elementary ¹³¹mXe was evaluated for a series of periodates.

Variation of bound xenon yield were observed during ¹³¹Xe concentration in crystals and during lithium periodate transition to cesium periodate.

67-19. Hagen, Georg

VIBRATIONS OF PLANAR SYMMETRICAL XY₄ MOLECULES WITH APPLICATION TO XENON TETRAFLUORIDE, *Acta Chemica Scandinavica* **21**, 465-72 (1967).

Symmetrized force constants (in mdyn/Å) are as follows: For species A_{1g}, F₁₁ = 3.2993; B_{1g}, 2.8199; B_{2g}, 0.0325; A_{2u}, 0.1500; B₂₇, 0.1366; E_u, F₁₁, 2.6534; F₂₂, 0.1211, F₁₂, -0.3397.

67-20. Haseltine, M. W., and H. C. Moser

OXIDATION OF RADON IN AQUEOUS SOLUTIONS, *J. Am. Chem. Soc.* **89**, 2497-8 (1967).

Various KBr₂ solutions were allowed to remain in contact with aqueous oxidizing solutions for days (at least 6 Rn half-lives). The solutions were then extracted with equal amounts of hexane. The lower rate of extraction from oxidizing solutions suggests conversion to a polar or ionic form. Flushing with air or argon gave similar results, whereas ion-exchange experiments suggest the oxidized Rn species as nonionic in neutral or acidic solution and anionic in strong alkaline solution. The results may be explained in terms of RnO₃ below pH 11 and HRnO₄⁻ above pH 11 in the aqueous oxidizing solutions. These results are obtained only when the Rn is allowed to come to equilibrium in the solution. Attempts to oxidize previously separated Rn were unsuccessful.

67-21. Harshbarger, W., R. K. Bohn, and S. H. Bauer

THE STRUCTURE OF KrF₂ AS INVESTIGATED BY ELECTRON DIFFRACTION, *J. Am. Chem. Soc.* **89**, 6466-9 (1967).

Electron diffraction patterns were recorded of a 40-kV beam scattered by the vapor in contact with a sample believed to be KrF₄ (maintained at -40°). The well-defined diffraction patterns were analyzed by conventional procedures and found to be produced by a mixture of KrF₂ and SiF₄. The symmetry of the diffractogram was established as O_h,h with (Kr-F) = 1.889 ± 0.010 Å. Electron diffraction patterns of an early (1963) sample of XeF₄ were analyzed and found to support the initial report based on these photographs that the symmetry of xenon hexafluoride was not that of a regular octahedron: (Xe-F)_{av} = 1.91 Å.

67-22. Holloway, John H.

EXPLOSION HAZARDS WITH XENON TRIOXIDE SOLUTIONS ("XENIC ACID"), *Talanta* **14**, 871-3 (1967).

Attention is drawn to the explosion hazards associated with xenic acid (xenon trioxide solution) and hence all xenon compounds that can yield xenon trioxide by hydrolysis.

67-23. Huston, J. L.

XENON DIOXIDE DIFLUORIDE: ISOLATION AND SOME PROPERTIES, *J. Phys. Chem.* **71**, 3339-41 (1967).

XeO₂F₂ can be conveniently prepared from XeO₃ and XeOF₄. The separation from the homogeneous liquid mixture of XeO₂F₂, XeO₄, and XeF₂ was followed with a time-of-flight mass spectrometer. The XeOF₄ is most volatile, the XeF₂ least volatile. The colorless crystals melt at 31°C to a colorless liquid. Although more stable than XeO₃, explosive decomposition has been observed. The infrared and Raman spectra are consistent with the predicted pseudo-trigonal bipyramid. Strong Raman bands at 537 cm⁻¹ and at 851 and 882 cm⁻¹ were assigned to symmetrical F-Xe-F stretching and Xe-O stretching, respectively; the infrared band at 610 cm⁻¹ was assigned to the unsymmetrical linear F-Xe-F stretch.

67-24. Jaselskis, B., T. M. Spittler, and J. L. Huston
PREPARATION AND PROPERTIES OF MONOCESIUM CHLOROXENATE (CsClXeO₃), *J. Am. Chem. Soc.* **89**, 2770 (1967).

The crystalline material is precipitated from cold, slightly alkaline aqueous solutions of acetonitrile on mixing CsCl and XeO₃ solutions. Although shock sensitive, it is more stable than XeO₃, evolving some Xe and O₂ at 150°C.

X-ray and infrared observations suggest a similarity to CsFXeO₃:

d spacings--4.03(w), 3.82(m), 3.34(m), 3.20(w), 2.68(m), 2.34(m), 2.00(s), and 1.74(w) Å.

IR absorption bands occur at: 818(s), 793(s), 766(m), 749(m), 663(w), and 400(m) cm⁻¹.

67-25. Jolly, William L.

INORGANIC SYNTHESIS WITH ELECTRIC DISCHARGES, *Amer. Chem. Soc., Div. Fuel Chem. Preprints*, Part 1 **11**(2), 125-7 (1967).

Electric-discharge reactions which yield thermodynamically unstable products are of interest to synthetic chemists, because such products are often difficult to prepare by other methods. Many fascinating compounds of unusual structure have been isolated from discharge reactions. Although such syntheses usually have low efficiencies, they are nevertheless of interest to chemists who hope to discover new types of compounds. The important types of electric discharges are discussed with particular emphasis on their use in lab syntheses. Some interesting compounds which have been prepared in electric discharges are B hydrides of large molecular weight, carboranes, O fluorides, NF₄AsF₆, and P₂Cl₄.

67-26. Jørgensen, Chr. Klixbüll

ELECTRONIC STRUCTURE AND MOLECULAR ORBITAL TREATMENT OF HALOGEN AND NOBLE GAS COMPLEXES IN POSITIVE, NEGATIVE AND UNDEFINED OXIDATION STATES, in "Halogen Chemistry," Vol. 1, 265-401. Ed. V. Gutmann, Academic Press, New York 1967.

An attempt at analysis and understanding of all reported observations, with particular emphasis on interpretation of absorption spectra.

67-27. Kirin, I. S., V. K. Isupov, V. I. Tikhonov, N. V. Ivannikova, Yu. K. Gusev, and G. G. Selikhov

USE OF XENON DIFLUORIDE FOR THE SYNTHESIS OF LABELED PERIODATES, Zh. Neorg. Khim. 12, 1088-9 (1967) translated by Elmar K. Wilip (ANL-Trans-538). 4p.

A labeled potassium periodate was prepared by the inter-formation of potassium iodate, labeled with the isotope ^{131}I , and xenon difluoride. The formation of oxygen compounds of ^{131}mXe during the β decay of ^{131}I in the synthesized potassium periodate has been established.

67-28. Kirin, I. S., and V. I. Tikhonov

PREPARATION OF XENON DIFLUORIDE LABELED BY RADIOACTIVE XENON, Radiokhimiya 9, 395 (1967). (In Russian.)

A method for the preparation of xenon difluoride under static conditions is described. The glass apparatus for the preparation is sketched.

67-29. Lefebvre, R.

PSEUDO-HYPERFINE INTERACTIONS IN RADICALS, Mol. Phys. 12, 417-26 (1967).

The pseudo-hyperfine interactions due to the combined effects of spin-orbit coupling and electron orbital-nuclear spin interaction may be important in a radical containing one or several heavy atoms. An expression is derived for these interactions using simple molecular orbital wave-functions. An estimate of the effect is made for the radical XeF trapped in a crystal of XeF_4 and values of the magnetic hyperfine coupling constants for the Xe nucleus are obtained which differ significantly from those originally proposed by Morton and Falconer.

67-30. Levine, Howard B. and George Birnbaum

CLASSICAL THEORY OF COLLISION-INDUCED ABSORPTION IN RARE-GAS MIXTURES, Phys. Rev. 154, 86-92 (Feb 1967).

Collision-induced far-infrared absorption has been observed experimentally in several rare-gas mixtures. A theoretical calculation of these spectra was carried out using classical radiation theory to determine the emission spectrum and converting to absorption via Kirchhoff's law. By using a simple empirical form to describe the variation of the collision-induced dipole moment with internuclear separation and by assuming straight-line collision paths, an analytic expression that agrees with experiments was obtained for the spectrum. Several elementary integrations permit analytical computation of the correlation function, relaxation time, static dielectric constant, and other invariants of the spectrum.

67-31. Malm, John G., and Evan H. Appelman

METAL PERXENATES, U.S. Patent No. 3,305,343, Feb. 21, 1967, 3 pp.

These compounds are prepared by alkaline hydrolysis of XeF_6 . Thus, a solution of 18 g NaOH in 80 ml H_2O is slowly added to 4.8 g XeF_6 at -195°C . The mixture is warmed to room temp and diluted with 80 ml H_2O . $\text{Na}_4\text{XeO}_6 \cdot 8\text{H}_2\text{O}$ (2 g) precipitates on standing for 12 hr. Alternative preparations include disproportionation of alkaline XeO_3 solutions and oxidation of such solutions with O_3 . The latter method gives normal perxenate with LiOH, RbOH, and CsOH, but $\text{K}_4\text{XeO}_6 \cdot 2\text{XeO}_3$ with KOH. Cu(III), Ag(II), La(III), Zn(II), Pb(IV), UO₂(II), and Th(IV) perxenate are precipitated by the addition of a soluble perxenate. Perxenate solutions have a characteristic UV absorption at 220-70 m μ . Alkaline solutions oxidize IO_3^- to IO_4^- , and Mn(II) to Mn(VII). Acid solutions are unstable and evolve O .

67-32. Margraff, R., and J. P. Adloff

ELECTROPHORETIC AND CHROMATOGRAPHIC BEHAVIOR OF XENIC ACID, J. Chromatogr. 26(2), 555-6 (1967) (French).

Electrophoretic and chromatographic data indicate that the hypothetical H_4XeO_6 exists in solution as either XeO_4^{4+} or XeO_2^{2+} . The electrophoretic data show that Xe migrates to the anode. No evidence was found of electrophoretic migration of Xe peroxide. The R_f values of the xenic acid anions is between 0.7 and 0.8 for the conditions tested.

67-33. Martin, Dominique

REACTIONS OF XENON DIFLUORIDE IN BROMINE TRIFLUORIDE SOLUTION, C. R. Acad. Sc. Paris, Ser. C 265, 919-22 (1967).

Both xenon difluoride and xenon tetrafluoride dissolve in bromine trifluoride without significantly ionizing (no added conductivity). The pentafluoride of phosphorus, arsenic and antimony do increase conductivity and they may be titrated conductimetrically with xenon difluoride solution with breaks suggesting complexes out of mole of xenon difluoride for 1 and 2 moles of PF_5 , and 1 mole of AsF_5 and SbF_5 each.

67-34. Maslov, O. D., V. A. Legasov, V. N. Prusakov, and B. B. Chaivanov

THE XeF_2 - SbF_5 BINARY SYSTEM, Zh. Fiz. Khim. 41(7), 1832-5 (1967) (Russian).

The following compounds were reported by a D.T.A. analysis of the mixture:

$\text{XeF}_2 \cdot 6\text{SbF}_5$ green, m. 34° forms a eutectic with SbF_5 at 2° ; $\text{XeF}_2 \cdot 2\text{SbF}_5$ yellow, m. 63° forms a eutectic with $\text{XeF}_2 \cdot 6\text{SbF}_5$ at 0.805 mole fraction SbF_5 at 25°C ; $\text{XeF}_2 \cdot 1.5 \text{ SbF}_5$ mustard yellow, m. 86.5° , eutectic at 0.625 mole fraction SbF_5 at 50°C ; $\text{XeF}_2 \cdot \text{SbF}_5$, mustard m. 161° eutectic at 0.57 mole fraction SbF_5 and 73.5° .

All compounds are soluble in SbF_5 , can be isolated as stable species; fluorine bridged structures are suggested.

67-35. Meinert, Hasso, and Gerhard Gnauck

FLUORIDES OF XENON AND KRYPTON, British Patent No. 1,056,657, Jan. 25, 1967, 2pp.

Xe or Kr is mixed with CF_2Cl_2 in a quartz vessel and subjected to a high-frequency discharge, by means of external electrodes, at 150-200 ma to form rare gas fluorides, which are collected in a cold trap. Recirculation of unreacted gases produces an almost quantitative yield.

67-36. Meinert, Hasso, and Stephan Rüdiger

THE CHEMISTRY OF NOBLE-GAS COMPOUNDS, The System Xenon Difluoride/Acetonitrile, (German) Z. Chem., 7-239 (1967).

The solubility is 16.8 g/100 ml at 0°C and 32.0 g/100 ml at 21°C. The solution is essentially non-conducting. The IR, Raman spectrum, and NMR are reported and interpreted in terms of no significant interaction. There is little decomposition at -10°C, but at 20°C the sample slowly deteriorates.

67-37. Meinert, Hasso, G. Kauschka, and S. Ruediger

CHEMISTRY OF INERT GAS COMPOUNDS.

I. REACTIONS OF XENON DIFLUORIDE AND XENON TETRAFLUORIDE WITH NONAQUEOUS SOLVENTS, Z. Chem. 7(3), 111-2 (1967) (German).

The reactions of XeF_2 and XeF_4 were studied in the non-aqueous solvents AsF_3 , IF_5 , NH_3 , SO_2 , CCl_3F , CCl_2F_2 , $\text{CCl}_3\text{FCClF}_2$, Me_2SO , $\text{C}_2\text{H}_5\text{N}$, and MeCN . XeF_2 or XeF_4 decomposed AsF_3 to evolve Xe and AsF_5 above the melting point of AsF_3 ; at room temp, the reaction was violent. At room temp XeF_4 reacted with IF_5 to form IF_7 , but XeF_2 showed no marked reaction at 20-50°C. XeF_4 and XeF_2 are insoluble in NH_3 from -78 to -33°C, but slowly evolve F and N to form NH_4F . XeF_2 is soluble in SO_2 from -72 to -10°C, but neither XeF_2 nor XeF_4 are soluble in CCl_3F or CCl_2F_2 . $\text{CCl}_3\text{F}-\text{CClF}_2$ reacts at room temperature with XeF_4 and XeF_2 to form mainly CClF_3 . XeF_4 and XeF_2 are soluble in Me_2SO and at ~30°C begin to evolve gas. $\text{C}_2\text{H}_5\text{N}$ reacts with XeF_4 or XeF_2 at room temperature with gas evolution. At room temperature, MeCN is not fluorinated by XeF_4 or XeF_2 , but near its boiling point, there is attack on the MeCN with the formation of fluorinated and oxidized products.

67-38. Micha, David A.

COMPOUND-STATE RESONANCES IN ATOM-DIATOMIC MOLECULE COLLISIONS, Phys. Rev. 162, 88-97 (1967).

The theory of atom-diatomic molecule collisions has been extended to include the coupling between open- and closed-channel states by means of the effective-Hamiltonian method as developed by Feshbach. The results have been used to discuss in detail compound-state resonances at energies below the first excitation threshold. Calculations are presented for the $\text{Xe} + \text{H}_2$ and $\text{Xe} + \text{D}_2$ systems. They suggest that compound-state resonances may be observable in molecular-beam experiments. These resonances are found to depend primarily upon the short-range anisotropic part of the interaction potential.

67-39. Mosevic, A. N., and J. Slivnik

EFFECTS OF PRESSURE, TEMPERATURE, AND MOLAR RATIO DURING SYNTHESIS OF XENON FLUORIDES, Nukl. Inst. Jozef Stefan, NIJS Porocilo 1967, P-203, 40 pp. (Slo).

At 120°C the reaction rate is just detectable, above 200° rather rapid. Excess of xenon yields mostly XeF_2 , excess fluorine (> 5:1) mostly XeF_6 , stoichiometric amounts rather pure XeF_4 . Vapor pressures of mixtures of fluoride can be estimated from cooling curves of the equilibrated reaction mixtures.

67-40. Mueller, Hans

MULTICENTER BONDING IN THE FREE-ELECTRON MODEL, Z. Chem. 7(3), 81-90 (1967) (German).

The quantum chemistry of multicentered bonding is developed for linear and cyclic atomic configurations on the basis of the free-electron model. Bond strengths, relative stabilities of various types of bonds, and electron distributions are discussed. The results obtained with the model compare well with the LCAO-MO descriptions. Multicentered bonding supplies a mechanism for describing organic molecules for which a 2-centered bonding description is inadequate. A number of specific examples are treated, e.g., H_2^+ , electron-pair bonding, O_2^- , B_2H_6 , H_3 , XeF_6 , ClF_3 , H_4 , and solid halogens.

67-41. Nefedov, V. D., M. A. Toropova, and A. V. Levchenko

β -DECAY OF ^{131}I AS A METHOD OF PREPARING ONIUM DERIVATIVES OF XENON, Radiokhimiya 9, 138-9 (1967). English Translation p. 136-7.

Diphenyliodonium perchlorate labeled with ^{131}I was allowed to decay in dilute aqueous solution and 10% HClO_4 solution. Only free xenon was found in the first case and ~40% bound xenon in the second.

67-42. Nelson, Leonard Y., and George C. Pimentel

INFRARED DETECTION OF XENON DICHLORIDE, Inorganic Chemistry 6, 1758 (1967).

A broad structured absorption band at 313 cm^{-1} is observed in the low temperature spectrum of a $\text{Xe}-\text{Cl}_2$ mixture passed through a microwave discharge. This is attributed to the asymmetric stretch of XeCl_2 with a force constant of 1.317 mdynes/\AA .

67-43. Pasternak, M.

MÖSSBAUER EFFECT STUDIES ON KRYPTON-83 IN BROMIDE AND BROMATE, Israel At. Energy Comm. 1967 (IA-1132), 22 pp. (English).

The Mössbauer effect was studied using ^{83}Kr sources produced by decay of ^{83}Br ($T_{1/2} = 2.4\text{ hr}$) in alkali metal bromide, potassium bromate, and $\text{Kr}-\beta$ -hydroquinone clathrate, and with solid krypton and the clathrate as absorbers. No evidence was found for an oxide formed from the bromate.

67-44. Pasternak, M., and T. Sonnino

MÖSSBAUER-EFFECT STUDIES ON ^{83}Kr IN BROMIDE AND BROMATE CRYSTALS, *Phys. Rev.* **164**, 384-90 (1967).

Mössbauer-effect studies have been performed using ^{83}Kr sources produced by the β^- decay of ^{83}Br ($T_{1/2} = 2.4\text{h}$) in various bromine compounds. Experiments were done with LiBr , NaBr , KBr , CsBr , NH_4Br , KBrO_3 , and $\text{Kr}-\beta$ -hydroquinone sources at 90°K using solid krypton absorber at 22°K . No isomer shift was observed for any of the sources, indicating that the Kr outer configuration is not perturbed by the induced dipole interaction with its neighbors. No " KrO_3 " species was detected as a result of the β^- decay of Br in KBrO_3 . Broad and symmetric emission lines were observed for the Kr-hydroquinone, the bromides, and the bromate, increasing in broadening in that order. This broadening has been explained on the basis of the formation of a local distorted crystalline field, as a consequence of the internal-conversion process of ^{83m}Kr . From the fact that a symmetric line is observed, it has been concluded that at least two modes of distortion are formed in such a way as to produce opposite signs of the electric field gradient. The Debye temperature calculated for the alkali-bromide sources was found to be 60°K in average, and for that of HN_4Br a value of 90°K was derived. The techniques of source preparation and of the krypton absorber deposition are described.

67-45. Pullen, Kent E., and George H. Cady

THE SYSTEMS XENON HEXAFLUORIDE-ARSENIC PENTAFLUORIDE AND XENON HEXAFLUORIDE-PHOSPHORUS PENTAFLUORIDE, *Inorg. Chem.* **6**, 2267-8 (1967).

In a system containing excess xenon, $2\text{XeF}_6\cdot\text{AsF}_5$ could be isolated while the $\text{XeF}_6\cdot\text{AsF}_5$ alone could be isolated with excess arsenic. Only the 2-1 compound $2\text{XeF}_6\cdot\text{PF}_5$ could be prepared whether the xenon or phosphorus fluoride was in excess.

67-46. Pullen, Kent Edward

PREPARATION AND PROPERTIES OF SOME COMPLEX COMPOUNDS OF XENON HEXAFLUORIDE, Thesis, University of Washington, 1967.

Xenon hexafluoride was found to react with stannic fluoride, germanium tetrafluoride, arsenic pentafluoride, and phosphorus pentafluoride to form the compounds $4\text{XeF}_6\cdot\text{SnF}_4$, $4\text{XeF}_6\cdot\text{GeF}_4$, $2\text{XeF}_6\cdot\text{GeF}_4$, $\text{XeF}_6\cdot\text{GeF}_4$, $2\text{XeF}_6\cdot\text{AsF}_5$, and $2\text{XeF}_6\cdot\text{PF}_5$. Where necessary or possible, the compounds were characterized by physical constants, chemical properties, chemical analysis, X-ray powder photographs, and infrared spectra.

67-47. Pullen, Kent E., and George H. Cady

THE SYSTEMS XENON HEXAFLUORIDE-GERMANIUM TETRAFLUORIDE AND XENON HEXAFLUORIDE-SILICON TETRAFLUORIDE, *Inorg. Chem.* **6**, 1300-2, 1967.

XeF_6 and GeF_4 , when mixed in the proper proportions, produce the compounds $4\text{XeF}_6\cdot\text{GeF}_4$, $2\text{XeF}_6\cdot\text{GeF}_4$, and $\text{XeF}_6\cdot\text{GeF}_4$. XeF_6 appears not to react with SiF_4 .

67-48. Reichman, Sandor, and John Overend

ABSENCE OF FERMI RESONANCE IN KRYPTON DIFLUORIDE, *J. Chem. Phys.* **47**, 3690 (1967).

The previously observed absence is explained in terms of a small bond-stretching force constant and the negative interaction force constant.

67-49. Rhodes, Harold J., and Martin I. Blake

XENON TRIOXIDE OXIDATION OF CERTAIN ALCOHOLS, *J. Pharm. Sci.* **56**, 1352 (1967).

A series of alcohols, aliphatic and aromatic, was oxidized with xenon trioxide. Oxidation to carbon dioxide and water was effected by adding a known excess of xenon trioxide to the reaction mixture. The excess reagent was determined iodometrically. Of the alcohols tested only triphenylcarbinol resisted oxidation. Essentially quantitative recoveries were obtained for ethanol, normal, secondary, and tertiary butyl alcohols, benzyl alcohol, benzohydrol, and cinnamyl alcohol.

67-50. Rhodes, Harold J., Ronald Kluza, and Martin I. Blake

OXIDATION OF BENZYL ALCOHOL AND BENZALDEHYDE WITH XENON TRIOXIDE, *J. Pharm. Sci.* **56**, 779-80 (1967).

PhCH_2OH is oxidized by XeO_3 in acidic or neutral solution to BzH and BzOH . The course of the reaction was followed by gas chromatography.

67-51. Selig, Henry

FLUORIDE CHEMISTRY OF THE NOBLE GASES, in "Halogen Chemistry," Vol. 1, 403-30, Ed. V. Gutmann, Academic Press, New York, 1967.

A comprehensive review (122 references).

67-52. Selig, Henry, and Arlene Mootz

THE ELECTRICAL CONDUCTIVITY AND DIELECTRIC CONSTANT OF LIQUID XeF_6 , *Inorg. Nucl. Chem. Letters* **3**, 147-8 (1967).

The dielectric constant of liquid XeF_6 at 55°C is 4.1. The electrical conductivity is $<10^6$ and is not significantly increased by the addition of CsF .

67-53. Studier, Martin H., and John L. Huston

GASEOUS OXIDES AND OXYACIDS OF IODINE AND XENON: MASS SPECTRA, *J. Phys. Chem.* **71**, 457-9 (1967).

Mass spectra were obtained for gaseous XeO_4 , XeO_3 , HIO_4 , HIO_3 , and I_2O_5 . There was no indication of the formation of lower Xe oxides, e.g., XeO or XeO_2 . XeO_3 samples were mounted on Pt filaments and electrically heated in the mass-spectrometer source. Peaks were observed for Xe^+ , XeO^+ , XeO_2^+ , and XeO_3^+ , but none indicated the presence of the lower oxides or oxyacids of Xe, e.g., H_2XeO_4 . Molecular distillation of 20-mg samples of XeO_3 gave 50-75% recoveries. HIO_4 and HIO_3 , formed as independent species, were identified from the spectrum of HIO_4 . I_2O_5 was not formed. Dehydrating HIO_3 and subsequent heating of the sample mounted on the filament caused sufficient

volatilization of I_2O_5 to give its mass spectrum. No lower oxides were formed, but IO^+ , IO_2^+ , and the dimeric I species were present.

67-54. Vasilescu, I. J.

EXISTENCE, STRUCTURE, AND PROPERTIES OF RADON COMPOUNDS, *Rev. Roum. Chim.* **12**, 835-8 (July 1967).

The heats of formation of radon chloride and fluorides were estimated according to a method worked out by Pitzer. The following values were calculated: $\Delta H_{\text{RnCl}_2} = -7.6$ kcal/mole, $\Delta H_{\text{RnF}_2} = -75$ kcal/mole, and $\Delta H_{\text{RnF}_4} = -86$ kcal/mole. The structure and some physicochemical properties of these compounds and other potential radon compounds are discussed.

67-55. Wilkins, C. J.

THE CHEMISTRY OF THE INERT GASES, J. N. Z. *Inst. Chem.* **31**, 11-17 (1967).

A discussion of the history and structure of the rare gas compounds.

67-56. Zeilenga, Gerald Raymond

PREPARATION AND REACTIONS OF SOME PENTA-FLUOROSULFANYL NITROGEN COMPOUNDS. SOME REACTIONS OF XENON, XENON HEXAFLUORIDE, AND SODIUM PERXENATE, Thesis, Purdue University, 1967.

A number of reactions were studied involving compounds which contain the SF_5N -group. Improved methods were developed for preparing $\text{SF}_5\text{N}=\text{SF}_2$. Some reactions of $\text{SF}_5\text{N}=\text{SF}_2$ and SF_5NH_2 were studied. The new compound SF_5NCl_2 was prepared by the reaction of NSF_3 and ClF .

A number of reactions of xenon, XeF_6 and Na_4XeO_6 were studied in attempts to prepare new xenon compounds.

1968

68-1. Adloff, J. P., and J. J. Schleiffer

RETENTION OF FLUORINE 18 PRODUCED BY THE $^{19}\text{F}(\text{n},\text{n})$ REACTION IN SOLID XeF_2 AND XeF_4 , *Inorg. Nucl. Chem. Letters* **4**, 403-5 (1968).

In XeF_2 the retention is complete, and in XeF_4 , $89 \pm 2\%$ of the fluorine is retained.

68-2. Bartlett, L. S.

MOLECULAR GEOMETRY, *J. Chem. Educ.* **45**, 754-67 (1968).

A discussion of molecular geometry in terms of non-bonded interactions. The valence-shell-electron-pair-repulsion model is compared with molecular orbital approximation. Noble-gas fluorides are considered at length.

68-3. Bartlett, L. S., and R. M. Gavin, Jr.

MOLECULAR STRUCTURE OF XeF_6 . II. INTERNAL MOTION AND MEAN GEOMETRY DEDUCED ELECTRON DIFFRACTION, *J. Chem. Phys.* **48**, 2466-83 (1968).

The distribution of internuclear distances in gaseous

XeF_6 exhibits unusually diffuse XeF_6 bonded and F-F geminal nonbonded peaks, the latter of which is severely skewed. The distribution proves the molecule cannot be a regular octahedron vibrating in independent normal modes. The instantaneous molecular configurations encountered by the incident electrons are predominantly in the broad vicinity of C_{2v} structures conveniently described as distorted octahedra in which the xenon lone pair avoids the bonding pairs. In these distorted structures the XeF bond lengths are distributed over a range of approximately 0.08 \AA with the longer bonds tending to be those adjacent to the avoided region of the coordination sphere. Fluorines suffer angular displacements from octahedral sites which range up to 5 or 10° in the vicinity of the avoided region.

Alternative interpretations of the diffraction data are developed in detail, ranging from models of statically deformed molecules to those of dynamically inverting molecules. In all cases it is necessary to assume that t_{1u} bending amplitudes are enormous and correlated in a certain way with substantial t_{2g} deformations. Notwithstanding the small fraction of time that XeF spends near O_h symmetry, it is possible to construct a molecular potential-energy function more or less compatible with the diffraction data in which the minimum energy occurs at O_h symmetry. The most notable feature of this model is the almost vanishing restoring force for small t_{1u} bending distortions. Indeed, the mean curvature of the potential surface for this model corresponds to a v_4 force constant F_{44} of $10^{-2} \text{ mdyne/\AA}$ or less. Various rapidly inverting non- O_h structures embodying particular combinations of t_{2g} and t_{1u} deformations from O_h symmetry give slightly better radial distribution functions, however. In the region of molecular configuration where the gas molecules spend most of their time, the form of the potential-energy function required to represent the data does not distinguish between a Jahn-Teller first-order term or a cubic V_{445} term as the agent responsible for introducing the t_{2g} deformation. The Jahn-Teller term is consistent with Goodman's interpretation of the molecule. On the other hand, the cubic term is found to be exactly analogous to that for other molecules with stereochemically active lone pairs (e.g., SF_6 , ClF_3). Therefore, the question as to why the XeF_6 molecule is distorted remains open. The reported absence of any observable gas-phase paramagnetism weighs against the Jahn-Teller interpretation.

The qualitative success but quantitative failure of the valence-shell-electron-pair-repulsion theory is discussed and the relevance of the "pseudo-Jahn-Teller" formalism of Longuet-Higgins *et al.* is pointed out. Brief comparisons are made with isoelectronic ions.

68-4. Bartlett, Neil

THE OXIDIZING PROPERTIES OF THE THIRD TRANSITION SERIES HEXAFLUORIDES AND RELATED COMPOUNDS, *Angew. Chem., Internat. Edit.* **7**, 433 (1968).

Some of the transition metal hexafluorides demonstrate an astonishing oxidizing power. In particular may be mentioned PtF_6 , which is capable of oxidizing molecular oxygen or xenon, a process requiring an electron affinity, $E(\text{PtF}_6) > -156 \text{ kcal mole}^{-1}$. From a comparative study of all of the hexafluorides of the third

transition series the electron affinity is seen to increase regularly in the sequence $WF_6 < ReF_6 < OsF_6 < IrF_6 < PtF_6$. The increase in E with unit increase in atomic number of M appears to be ~ 20 kcal mole $^{-1}$. On the other hand, the ability of the hexafluorides to accept F^- decreases along this series. This effect enables IrF_6 to be more effective than PtF_6 in the generation of ONF_2 by the oxidative fluorination of ONF . Both PtF_6 and IrF_6 interact spontaneously with ONF or O_2NF to generate fluorine, at or below room temperature. The decrease in F^- -acceptor ability along the series, which stands in sharp contrast to the increase in electron affinity, suggests that ligand crowding increases sharply across the series from WF_6 to PtF_6 . This accords with the observed decrease in molecular volume along the series, both in the hexafluorides and in the MF_6^- salts. It is clear from this comparison that the species IrF_6 and PtF_6 are close to a minimum volume for this series. The oxide pentafluorides $ReOF_5$ and $OsOF_5$ are similar in oxidizing ability to their respective hexafluorides, but are poorer F^- acceptors. Evidently the ligand crowding in MOF_5 molecules is greater than in MF_6 .

68-5. Bartlett, N., and F. O. Sladky

XENON DIFLUORIDE AS AN OXIDATIVE FLUORINATOR, Chem. Comm. **1968**, 1046-7 (1968).

XeF_2 is a useful oxidative fluorinator in solvents such as BrF_3 , CH_3CN , and HF , and may be dissolved and maintained even in dry SO_2 . Acid (or H_2O which yields HF) catalyzes reactions, e.g., with I_2 . The reaction with $Y-SO_3$ offers an attractive synthesis of $S_2O_6F_2$.

68-6. Bartlett, N., and F. O. Sladky

THE RELATIVE FLUORIDE ION DONOR ABILITIES OF XeF_2 , XeF_4 , AND XeF_6 AND A CHEMICAL PURIFICATION OF XeF_4 , J. Am. Chem. Soc. **90**, 5316-7 (1968).

XeF_6 is a strong fluoride ion donor, XeF_2 is a weaker donor, and XeF_4 shows no donor abilities. In the presence of AsF_5 , the donors are much less volatile, and XeF_4 may be relatively pure by sublimation.

68-7. Binenboym, Jehuda, Henry Selig, and Jacob Shamir

A XENON DIFLUORIDE-ARSENIC PENTAFLUORIDE COMPLEX, J. Inorg. Nucl. Chem. **30**, 2863-5 (1968).

The compound $XeF_2 \cdot AsF_5$ is a white, slightly volatile solid melting to a yellow liquid between 75 and 80°. It is soluble in anhydrous hydrogen fluoride to form a non-conducting solution. The infrared spectrum of the solid (strong band at 675 cm^{-1} and weak band at 565 cm^{-1}) is interpreted in terms of a non-ionic molecular adduct, possibly fluorine bridged. Some crystals were indexed as tetragonal with $a = 7.79$ and $c = 5.56$ Å.

68-8. Claassen, Howard H., Earl L. Gasner, Hyunyong Kim, and J. L. Huston

VIBRATIONAL SPECTRA AND STRUCTURE OF XeO_2F_2 , J. of Chem. Phys. **49**, No. 1, 253-7, July 1968.

The Raman spectra of liquid and solid XeO_2F_2 and the

infrared spectrum of XeO_2F_2 in an argon matrix at liquid-helium temperature are reported. They are interpreted in terms of C_{2v} molecular symmetry which can be associated with a molecule of pseudobipyramidal structure, where the two F atoms are axial to the Xe and the two O atoms with a lone electron pair are equatorial. The vibrational spectra support the existence of primarily monomeric XeO_2F_2 molecules in the liquid state and quite probably in the solid. The nine fundamentals assigned are: 848 (ν_1), 490 (ν_2), 333 (ν_3), 198 (ν_4), 224 (ν_5), 905 (ν_6), 324 (ν_7), 585 (ν_8), and 317 (ν_9).

68-9. Cyvin, S. J., B. N. Cyvin, A. Mueller, and B. Krebs

VIBRATIONS OF MOLECULES AND IONS OF THE TYPE XY_4 WITH D_{4h} SYMMETRY AND MASS DEPENDENCE OF CORIOLIS COUPLING CONSTANTS, Z. Naturforsch., A1968 **23**(4), 479-81 (German).

Mean bond-vibration amplitudes at 0 and 298°K, force constants, and Coriolis coupling constants, were calculated from known IR frequency data for molecules and ions of the type XY_4 with D_{4h} symmetry, e.g., $PdCl_4^{2-}$, XeF_4 , $AuBr_4^-$, and $Pt(NH_3)_4^{2+}$. The well-defined mass-dependence of the Coriolis coupling constants is demonstrated.

68-10. Davis, B. H., J. L. Wishlade, and P. H. Emmett

THE REACTIONS OF XENON AND FLUORINE TO FORM XENON FLUORIDES, J. Catal. **10**(3), 266-71 (1968).

The reactions of Xe with F are heterogeneous and occur for the most part on the fluorinated walls of the Monel reaction vessels or on the surface of added metal fluorides.

CoF_3 , NiF_2 , and CaF_2 all exhibited catalytic activity for the F-Xe reactions.

68-11. Falconer, W. E., Alfred Büchler, James L. Stauffer, and William Klemperer

MOLECULAR STRUCTURE OF XeF_6 AND IF_7 , J. Chem. Phys. **48**, 312 (1968).

The deflection of molecular beams of XeF_2 , XeF_4 , XeF_6 , and IF_7 in an inhomogeneous electric field has been examined. From the defocusing behavior of each of these species, it is concluded that the electric dipole moment μ is less than 0.03 D for XeF_4 , XeF_6 , and IF_7 if these molecules have rigid structures. The upper limit for the polarity of nonrigid (inverting) structures is $(\mu/\Delta^{1/2}) < 0.1$ D/(cm^{-1}) $^{1/2}$, where Δ is the separation between inversion doublets. These results imply molecular structures with symmetry-forbidden electric-dipole moments for XeF_4 , XeF_6 , and IF_7 .

68-12. Feher, Istvan, and Maria Lorinc

REACTION OF XENON DIFLUORIDE WITH WATER, Magy. Kem. Foly. **1968** **74**(5), 232-4 (Hungarian).

The rates of hydrolysis of XeF_2 were determined at 0 and 25°C, by three different methods, namely, by radioactive-tracer technique with labeled XeF_2 , volumetric analysis of the O and Xe gas products, and electric-conductivity measurement of the HF solution produced. The hydrolysis occurs according to the reaction $XeF_2(soln) + H_2O - (OH^-) \rightarrow Xe(gas) + 0.5 O_2 +$

2HF(soln). In the first method, using ^{133}Xe and $^{133\text{m}}\text{Xe}$ tracers, the reaction in the XeF_2 solution was measured after removal of the Xe gas, by determining residual activity. All three methods have one common fault, namely, that while the solid XeF_2 is being dissolved, concentration changes are uncontrolled and a heterogeneous dissociation can occur on the surface of the XeF_2 crystals. Since the rate of dissolution is much greater than the rate of reaction, only about 5% of the XeF_2 reacts. The error in these methods is 1-5%, depending on the concentration of the solution. The reaction proved to be of first-order; the rate constant, as evaluated from the measured values of any of the reaction products, is uniformly $1.7 \pm 0.1 \times 10^{-3} \text{ min}^{-1}$ at 0 and $1.51 \pm 0.04 \times 10^{-2} \text{ min}^{-1}$ at 25°C . No electrolytic dissociation of XeF_2 could be observed in the aqueous system. The results provide information concerning the mechanism of the reaction of XeF_2 with water and about the toxicity of XeF_2 .

68-13. Felix, F. W.

RARE-GASES IN SOLIDS. XXXIX. RARE-GAS DIFFUSION IN NEUTRON-IRRADIATED RUBIDIUM HALIDES, *Phys. Status Solidi* 1968 27(2), 529-34.

The release of radioactive Kr from neutron-irradiated single crystals of Rb halides was measured from 150°C up to the melting point. The release behavior is similar to earlier results with the K halides. The activation energies for RbCl , RbBr , and RbI at higher temp are 0.56, 0.30, and 0.31 eV, respectively. Kr diffuses by an interstitial mechanism. At lower temp, a stronger dependence is found, which is attributed to the interaction of the gas atoms with defects. The activation energies in this region are 2.04, 1.68, and 1.41 eV, respectively. RbF shows only a single activation energy of 1.38 eV. In RbI the simultaneous diffusion of Kr and Xe was investigated.

68-14. Flohr, Kathleen, and Evan H. Appelman

THE RESISTANCE OF RADON TO OXIDATION IN AQUEOUS SOLUTION, *J. Am. Chem. Soc.* 90, 3584 (1968).

The observations of Haseltine and Moser are probably due to trapping of radon in less soluble radium compounds. No evidence was found for the existence of radon compounds.

68-15. Gavin, R. M., Jr., and L. S. Bartell

MOLECULAR STRUCTURE OF XeF_6 . I. ANALYSIS OF ELECTRON-DIFFRACTION INTENSITIES, *J. Chem. Phys.* 48, 2460-5 (1968).

A gas-phase electron-diffraction investigation of xenon hexafluoride has been carried out in an effort to obtain structural information which might shed light on the curious properties of the compound. Elaborate precautions were taken to prevent decomposition or contamination of the sample (99.8 mole % pure). Several innovations were introduced into the structure analysis to minimize difficulties encountered in conventional analyses of molecules containing both heavy and light atoms. Two different sets of analyses (I and II) employing two different levels of approximation in electron scattering theory were conducted to test the adequacy of the expressions usually adopted. Analysis I was based on Hartree-Fock x-ray

elastic scattering factors, Heisenberg-Bewilogua inelastic scattering factors, and (modified) Born phase-shift corrections for Thomas-Fermi atomic fields. Improvements in Analysis II included the new electron elastic scattering factors and Born phase-shift corrections calculated by the partial wave method by Cox and Bonham, and Hartree-Fock inelastic scattering factors. The Hartree-Fock phase-shift correction was not in complete agreement with experiment but was markedly better than the Thomas-Fermi correction. The effect of ionic character on phase shift was investigated theoretically and shown to be significant. A mean Xe-F bond length of $1.890 \pm 0.005 \text{ \AA}$ was found, but the radial distribution function for Xe-F bonds corresponded to that of a composite for nonequivalent bonds. Amplitudes of bending oscillations are notably large. The diffraction data are not compatible with a regular octahedral XeF_6 molecule vibrating in independent normal modes. A more detailed exposition of alternative structures and internal motion is presented in Paper II.

68-16. Glass, W. K.

THE GAS-PHASE STRUCTURE OF XENON HEXAFLUORIDE, *Chem. Comm.* 1968, 455 (1968).

The molecule was analyzed on the basis of previously published data. It is suggested that the ground-state vapor molecules of XeF_6 possess O_h symmetry, but have unusual electronic properties which markedly influence band widths.

68-17. Huston, J. L.

XENON TRIOXIDE DIFLUORIDE: MASS SPECTRUM, *Inorg. Nucl. Chem. Letters* 4, 29-30 (1968).

Xenon trioxide difluoride was observed in a mass spectrometer as a volatile product of the reaction of xenon hexafluoride and sodium perxenate.

68-18. Hyunyoung, Kim, Paul A. Souder, and Howard H. Claassen

MOLECULAR FORCE FIELDS OF OCTAHEDRAL XF_6 MOLECULES, *J. Mol. Spectroscopy* 26, 46-66 (1968).

The orbital valency force field (OVFF) was applied to the fifteen hexafluorides whose vibrational frequencies are known, and the best-fit force constants were calculated. The OVFF showed definite advantages over the more widely used UBFF model in that (a) the angular coordinates contain no redundancy; (b) the agreement with the observed frequencies in the angle deformation modes is far superior; and (c) the least-squares calculation procedure yields rapidly converging sets of force constants for all fifteen hexafluorides. The f_{111} force constants of some of the hexafluorides were determined from their infrared-band envelopes and were compared with the calculated values. The angle distortion constant D and the repulsion constant F were found to have strong dependence upon the number of nonbonding electrons in the 4d and 5d transition metal series. This effect is discussed in terms of the repulsion between the nonbonding and bonding electrons and the Coulombic forces between partially ionic fluorine atoms.

68-19. Martins, Joseph F., and E. Bright Wilson, Jr.

THE MICROWAVE SPECTRUM, MOLECULAR STRUCTURE AND DIPOLE MOMENT OF XENON OXYTETRAFLUORIDE, *J. Mol. Spectroscopy* **26**, 410-17 (1968).

Refined values of the structural parameters of xenon oxytetrafluoride have been obtained from the microwave spectrum: $r(\text{Xe}-\text{O}) = 1.703 \pm 0.015 \text{ \AA}$, $r(\text{Xe}-\text{F}) = 1.900 \pm 0.005 \text{ \AA}$, $\angle (\text{O}-\text{Xe}-\text{F}) = 91.8 \pm 0.5^\circ$. The dipole moment was measured by double resonance to be $0.65 \pm 0.09 \text{ D}$. Lines from three vibrational satellites were seen and a partial assignment was made.

68-20. Murchison, Craig, Sandor Reichman, Dennis Anderson, John Overend, and Felix Schreiner
THE STRUCTURE OF KRYPTON DIFLUORIDE, *J. Am. Chem. Soc.* **90**, 5690-3 (1968).

The band at ca. 590 cm^{-1} in the infrared spectrum of $^{86}\text{KrF}_2$ has been studied with a resolution of 0.08 cm^{-1} . From the rotational fine structure it is clear that KrF_2 is a linear molecule and the two fluorine atoms are symmetrically equivalent. The analysis of the band gives $v_0 = 589.889$, $B_0 = 0.12626$, $B' = 0.12575$, and $D_0 = D' = 7.8 \times 10^{-8} \text{ cm}^{-1}$ as the most probable set of constants, although we cannot rule out a second set of constants corresponding to an alternative assignment. From these results we conclude that the length of the KrF bond, r_0 , is equal to $1.875 \pm 0.002 \text{ \AA}$, or possibly $1.867 \pm 0.002 \text{ \AA}$.

68-21. Musher, Jeremy I.

ORGANIC ESTERS OF XENON, *J. Am. Chem. Soc.* **90**, 7371-2 (1968).

When solid XeF_2 is added to excess trifluoroacetic acid, solid silver trifluoroacetate, and solid sodium acetate, a relatively non-volatile product is obtained which gives a mass spectrum containing xenon and not xenon fluoride fragments.

68-22. Perlow, G. J., and M. R. Perlow

STUDIES OF XENON CHLORIDES AND OTHER XENON COMPOUNDS BY THE MOESSBAUER EFFECT IN ^{129}Xe , *J. Chem. Phys.* **48**, 955-61 (1968).

The compounds XeCl_2 and XeCl_4 have been made in the beta decay of ICl_2^- and ICl_4^- containing radioactive ^{129}I . The electric-quadrupole interaction in the 39.6-keV excited state of the ^{129}Xe nucleus was employed to study these substances by the Mössbauer effect. The decay products are compared with XeF_2 , XeF_4 , and with the parent ions. It is shown that the decays $\text{ICl}_2^- \rightarrow \text{XeCl}_2$ and $\text{ICl}_4^- \rightarrow \text{XeCl}_4$ both result in the recall of 0.2 electron per bond from each ligand to the central atom. In the xenon halides the charges per fluorine are -0.72 and per chlorine are -0.5. The assumption of pure p_σ bonding in the xenon halides was tested by the isomer shifts. With its aid the shifts can be calibrated by the quadrupole couplings. A shielding constant obtained from Hartree-Fock calculations by Wilson was then used to relate p -electron to s -electron transfer, which was next employed to examine the charges on the xenon atom in XeO_4 and XeO_6^{4-} . The former is prepared in beta decay, the latter equivalently either in beta decay or in bulk. It was shown that directed sp^3d^2 hybrid bonds for XeO_6^{4-}

are inconsistent with the measured isomer shift. The recoilless fractions and linewidths are tabulated for a number of xenon compounds.

68-23. Schreiner, Felix, Geraldine N. McDonald, and Cedric L. Chernick

THE VAPOR PRESSURE AND MELTING POINTS OF XENON DIFLUORIDE AND XENON TETRAFLUORIDE, *J. Phys. Chem.* **72**, 1162 (1968).

Vapor-pressure measurements have been carried out with samples of pure XeF_2 and XeF_4 . The preparation and purification of the samples are described, as well as the apparatus with which the data for the two reactive fluorine compounds were obtained. For XeF_2 , the following equation represents the experimental results between 273 and 388°K :

$$\log P_{\text{mm}} = -\frac{3057.67}{T} - 1.23521 \log T + 13.969736.$$

The corresponding vapor pressure equation for XeF_4 , valid between 275 and 390.25°K , is

$$\log P_{\text{mm}} = -\frac{3226.21}{T} - 0.43434 \log T + 12.301738.$$

In addition, the triple-point temperatures of the two compounds have been determined by a thermal-arrest method. For XeF_2 a triple-point temperature of 402.18°K was found, and for XeF_4 , 390.25°K . The enthalpies of vaporization at 330°K were derived from the vapor-pressure equations; the following values were obtained: $\Delta H_{\text{sub}} = 55.2 \pm 0.8 \text{ kJ mole}^{-1}$ for XeF_2 , and $\Delta H_{\text{sub}} = 60.6 \pm 1.0 \text{ kJ mole}^{-1}$ for XeF_4 . The standard entropy of XeF_4 vapor at 298.15°K was calculated from the vapor pressure and heat capacity data, and found to be $305.2 \text{ J deg}^{-1} \text{ mole}^{-1}$. This number is compared with the entropy calculated from molecular data. The entropy of solid XeF_2 at 330°K was calculated to be $122.8 \text{ J deg}^{-1} \text{ mole}^{-1}$.

68-24. Sladky, F. O., P. A. Bulliner, and N. Bartlett
XENON DIFLUORIDE AS A FLUORIDE ION DONOR AND THE CRYSTAL STRUCTURE OF $[\text{Xe}_2\text{F}_3]^+[\text{AsF}_6]^-$, *Chem. Comm.* **1968**, 1048-9 (1968).

Three adduct types are found between XeF_2 and noble-metal pentafluorides: $2\text{XeF}_2\cdot\text{MF}_5$, $\text{XeF}_2\cdot\text{MF}_5$, and $\text{XeF}_2\cdot 2\text{MF}_5$, where $\text{M} = \text{Pt, Ir, Ru, and Rh}$. The 1:2 adduct is not found with AsF_5 . On the basis of Raman and IR spectroscopy and an X-ray structure for the 1:2 AsF_5 complex these are formulated as $[\text{Xe}_2\text{F}_3]^+[\text{MF}_6]^-$, $[\text{XeF}]^+[\text{MF}_6]^-$, and $[\text{XeF}]^+[\text{M}_2\text{F}_{11}]^-$; xenon difluoride as an oxidative fluorinator. Xenon difluoride dissolves very readily in BrF_3 , BrF_5 , and IF_5 , and in the absence of water or HF in acetonitrile and SO_2 . The XeF^+ or Xe_2F_3^+ are postulated as active intermediates in reaction with iodine or gamma sulfatrioxide.

68-25. Slivnik, J., A. Šmalc, B. Žemva, and A. N. Mosevič

ON THE SYNTHESIS OF XENON DI-, TETRA-, AND HEXAFLUORIDE, *Croat. Chem. Acta* **40**, 49-51 (1968).

Experiments are reported on heating a mixture of F and Xe (30:3 atm at 22°C) in closed Monel vessels at 120, 150, and 200°C . At each temp the pressure, as measured with a Bourdon gauge at room temp, was

dropping and after some time equilibrated yielding compounds of calculated compositions: $\text{XeF}_{1.90}$, $\text{XeF}_{4.04}$, and $\text{XeF}_{6.05}$. The solid product, obtained upon cooling to 22°C , was analysed by hydrolysis and titration with $\text{Th}(\text{NO}_3)_4$. The contents of F in each was found: 22.2, 37.0, and 46.4%, respectively.

68-26. Venkateswarlu, K., and Joseph K. Babu
FORCE FIELD, CORIOLIS COUPLING COEFFICIENTS,
GENERALIZED MEAN SQUARE AMPLITUDES OF
VIBRATION, AND SHRINKAGE CONSTANTS OF XeF_4
AND XeOF_4 , Acta Phys. Acad. Sci. Hung. 24(1), 95-101,
(1968).

Normal-coordinate analyses of XeF_4 and XeOF_4 were carried out by using the general valence and Urey-Bradley force fields, respectively. The Coriolis coupling coefficients, generalized mean square amplitudes, and shrinkage constants were also evaluated. The values obtained in both cases are discussed in relation to each other. The perpendicular mean square amplitudes (ΔZ^2) and (Δy^2) associated with the Xe-F and Xe-O bonds are greater than the corresponding (Δz^2) values. The parallel mean square amplitude of Xe-F in XeOF_4 is a little lower than in XeF_4 . This

lowering in the value of (Δz^2) of Xe-F may be due to the increase in the charge on Xe owing to the bonding Xe-O. According to the simple treatment of bonding in Xe fluorides (N. Bartlett, 1964), there are 2 non-bonding electron pairs above and below the Xe-F₄ plane in XeF_4 . One of these pairs is utilized in the bonding Xe-O, with a consequent increase of charge on Xe. This increased charge reduces the amplitude of the Xe atom leading to a lowering of the Xe-F (Δz^2) value. The shrinkage constants are different in the 2 molecules.

68-27. Yeranov, Walter A.

PREDICTED ROOT-MEAN-SQUARE AMPLITUDES OF
XENON TETROXIDE, Z. Naturforsch., A1968 23(4),
618-20.

A theoretical analysis of the mean amplitude of vibrations of XeO_4 is presented. The calculation of the root-mean-square amplitudes of vibration (l_e) of the bonded and the nonbonded interatomic distances of XeO_4 are reported. The values of $l_e(\text{Xe}=\text{O})$ and $l_e(\text{O} \cdots \text{O})$ are 0.00550903 Å and 0.0742 Å, respectively, (sic) at 298°K .

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